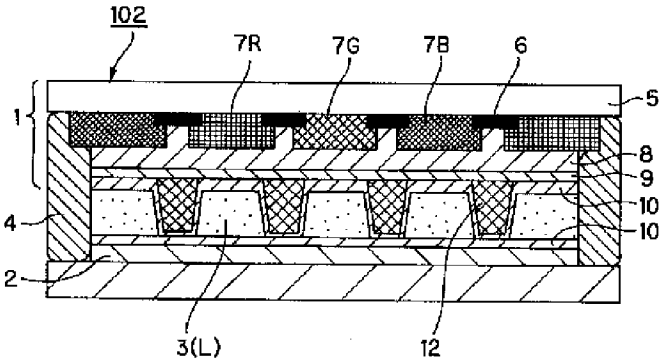
JAPANESE [JP,2001-106765,A]

[Translation done.]

Drawing selection Representative draw



[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the hardenability resin compositions of the high sensitivity containing the hardening resin of high sensitivity with possible making it harden with a small light exposure, and the hardening resin concerned, and those manufacturing methods.
[0002]Sensitivity this invention to a high thing in addition, during during preservation, use, or handling, The high stability resin which cannot cause easily increase of the molecular weight which is not desired, and the increase in viscosity (for example, photo-setting resin with good preservability), The hardening resin which has the high sensitivity concerned and high stability is contained, and regulation and equalization of the thickness of a coating film are related also with easy hardenability resin compositions and those manufacturing methods, without causing the increase in viscosity in preservation or coating.
[0003]This invention relates also to the high sensitivity containing high sensitivity and transparent hardening resin, and the hardening resin concerned, transparent hardenability resin compositions, and those manufacturing methods.
[0004]Furthermore, this invention relates also to few light filters and liquid crystal panels of color unevenness or contrast nonuniformity in which the spacer of the protective film which covers a coloring layer and the coloring layer concerned using the hardenability resin composition of the above-mentioned high sensitivity, or the liquid crystal layer was formed.
[0005]
[Description of the Prior Art]In recent years, a color liquid crystal display is spreading quickly as flat displays, such as a personal computer.

Generally, as shown in drawing 1, the color liquid crystal display (101) made the light filter 1 and the electrode substrates 2, such as a TFT substrate, counter, formed the about 1-10-micrometer interval part 3, was filled up with the liquid crystal compound L in the interval part 3 concerned, and has taken the structure which sealed the circumference by the sealant 4. The black matrix layer 6 formed in the predetermined pattern in order that the light filter 1 might shade the boundary part between pixels on the transparent substrate 5, In order to form each pixel, [the coloring layer 7 or these days] which arranged two or more colors (usual, three principles of red (R) green (G) blue (B)) to specified order, the light filter, the protective film 8, and the transparent electrode film 9 have taken the structure laminated sequentially from [this] the side near a transparent substrate. The orienting film 10 is formed in the inner surface side of the light filter 1 and this, and the electrode substrate 2 that counters. Furthermore, in order to maintain uniformly and uniformly the cell gap between the light filter 1 and the electrode substrate 2, the pearl 11 which has fixed particle diameter as a spacer is distributed by the interval part 3. And a color picture is obtained by controlling the light transmittance of the liquid crystal layer which is behind each pixel or light filter colored each color.

[0006]The protective film 8 formed in a light filter has played the role of protection of a coloring layer, and flattening of a light filter, when a coloring layer is provided in a light filter. The gap unevenness which originates in the wave of the transparent substrate surface of a light filter in a color liquid crystal display, When the surface smoothness of the transparent electrode film 9 is spoiled by existence of the gap unevenness between each pixel of R, G, and B or the gap unevenness within each pixel, color unevenness or contrast nonuniformity is produced and, as a result, there is a problem referred to as causing deterioration of imaging quality. Therefore, a protective film is asked for high surface smoothness.

[0007]In distributing the pearl 11 of the shape of a particle as shown in drawing 1 as a spacer, whether it is the back of the black matrix layer 6 or it is the back of a pixel distribute the pearl concerned at random not related. When the pearl has been arranged at the viewing area, i.e., a picture element part, the light of a back light penetrates the portion of a pearl, and the orientation of the liquid crystal of the pearl circumference is in disorder, and the grace of a display image is reduced remarkably. Then, forming the columnar spacer 12 which has the height corresponding to a cell gap in the position and weight **** field in which it is an inner surface side of a light filter, and the black matrix layer 6 is formed has come to be performed instead of distributing a pearl, as shown in drawing 2.

[0008]The above-mentioned protective film 8 and the columnar spacer 12 can be formed using resin. As for the protective film 8, when the adhesion and sealing nature of a seal part are taken into consideration, it is preferred that it is what can cover only the field in which the coloring layer on a transparent substrate was formed. It is necessary to form the columnar spacer 12 correctly in the inside of the formation area of a black matrix layer, i.e., non display regions. For this reason, a protective film and a columnar spacer came to be formed using the photo-setting resin which can limit easily the field which you want to harden with a photo mask.

[0009]Since it is complicated in respect of handling and waste liquid treatment and economical efficiency and stability are missing when

negatives are developed using an organic solvent after exposing the coating surface of a photo-setting resin in order to form a protective film and a columnar spacer, An acidic group is introduced into a photo-setting resin, and the photo-setting resin which could be made to carry out alkaline development after exposure is developed.

[0010]As an alkali solubility photo-setting resin, weight average molecular weight is known for o-cresolnovolak epoxy acrylate of about 2,000, etc., for example. This resin has a carboxylic acid group which specifies alkali solubility. However, since a monomer component is used for it as an acrylyl group which specifies hardenability, this resin has the low reliability at the time of membrane formation, for example, has fear of a residual monomer unit being eluted to a liquid crystal part, and further, there may be many elution volumes at the time of alkaline development, and may carry out a decrease film.

[0011]As a method of introducing radical polymerization nature groups, such as an acrylyl group, into the molecular structure of a compound, in order to give a photoresist, For example, make superfluous diisocyanate react to diol and the reactant which left the isocyanate group to the end is prepared, By making the isocyanate group of this reactant react to 2-hydroxyl ethyl methacrylate etc., and making urethane acrylate generate, the method of introducing radical polymerization nature groups, such as a methacryloyl group, into an end is known. However, in this method, an acrylyl group is theoretically introduced only into the both ends (meta) of molecular structure. How to make contain some compounds which have two or more radical polymerization nature groups, such as an acrylyl group (meta), and carry out a radical polymerization into a monad, is considered, and content of a radical polymerization nature group cannot be controlled, but there are also problems, such as gelling.

[0012]Thus, if you form the protective film and columnar spacer of a light filter using a photo-setting resin, it is convenient, but. In the conventional photo-setting resin, it was difficult to control the quantity of radical polymerization nature groups, such as alkali solubility groups, such as a carboxyl group, and an acrylyl group (meta), in consideration of the hardenability, alkali solubility, etc.

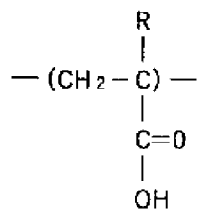
[0013]

[Problem(s) to be Solved by the Invention]According to the knowledge which was acquired by research of these people and which is not yet exhibited. It has a main chain which consists of a constitutional unit expressed with a following formula (1) at least, and a constitutional unit expressed with a following formula (2), The copolymerization resin which the (meth)acryloyloxy alkyl isocyanate compound of the carboxyl group or a hydroxyl group expressed with a following formula (5) in part at least combined by the reaction of the isocyanate group of the compound concerned, Since the quantity of the carboxyl group of alkali solubility and the acrylyl group (meta) of radical polymerization nature can be adjusted freely, it is dramatically suitable as a photo-setting resin.

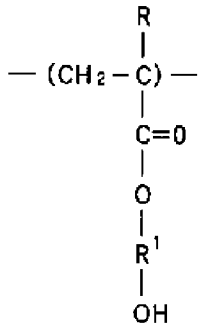
[0014]

[Formula 13]

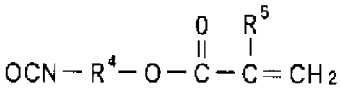
式 (1)



[0015]
[Formula 14]
式 (2)



[0016]
[Formula 15]
式 (5)



(Among each formula, the alkylene group of the carbon numbers 2-4 and R^4 show an alkylene group, and, as for R, R^5 shows hydrogen or methyl, as for hydrogen or the alkyl group of the carbon numbers 1-5, and R^1.) However, in order to form the coat and pattern of hardening resin using the above-mentioned copolymerization resin, raising sensitivity is called for so that the copolymerization resin concerned may harden promptly also with a small light exposure.

[0017]When the solvent was dissolved or distributed and the above-mentioned copolymerization resin was neglected, the molecular weight increased quickly and it became clear that viscosity rose. In our experiment, this thickening phenomenon advancing even at a room temperature, and going on so quickly that storage temperature being high is checked. In one experiment using GPC (Gel Permeation Chromatography, gel permeation chromatography), The above-mentioned copolymerization resin was dissolved in the solvent, the molecular weight which was 69,000 at the time of preparation increased even to 98,000 only by saving for two weeks at a room temperature, and the viscosity of the solution was set to 1.17. When this copolymerization resin was saved for three days at 70 **, the molecular weight which was 69,000 at the time of preparation increased even to 340,000, and the viscosity of the solution increased 2.14 times. a thickening phenomenon is the much more when saved in the state of the coating liquid which mixes this copolymerization resin with thermoset epoxy resin, an acrylic monomer, a polymerization initiator, etc., is dissolved in a solvent, and is actually used -- becoming remarkable is also checked. Since the above-mentioned copolymerization resin causes such a thickening phenomenon, preservability is missing and it is easy to produce coating nonuniformity.

[0018]The height of the columnar spacer for securing especially the thickness of the coloring layer of a light filter, the thickness of the protective film which covers the coloring layer concerned, and the cell gap of a liquid crystal panel is asked for very high accuracy and homogeneity. Since continuously forming is carried out to the field the

coloring layer and whose protective film settled, it receives and a columnar spacer is moreover intermittently formed in more than twice as many height as this compared with coloring layer thickness according to the formation area of a black matrix layer, it is easy to cause size fluctuations by viscosity increase of coating liquid. If resin for coating carries out polymers quantification too much, the shape of a columnar spacer will worsen and the intensity as a spacer and other mechanical properties will deteriorate. Therefore, to form the coloring layer and protective film of a light filter, a columnar spacer, especially a columnar spacer using the coating liquid of the photo-setting resin constituent containing the above-mentioned copolymerization resin, it is necessary to prevent the thickening phenomenon of coating liquid as much as possible.

[0019]Resin for forming the coloring layer and protective layer of a light filter is asked for good transparency. However, according to this invention persons' knowledge, the above-mentioned copolymerization resin is not necessarily provided with sufficient transparency.

[0020]This invention is finished in consideration of this situation, and the first purpose is to increase the method of raising the sensitivity of the above-mentioned hardenability copolymerization resin, and until now also, and to provide hardening resin with high sensitivity.

[0021]The second purpose of this invention is to provide the method of raising preservability and stability with the sensitivity of the above-mentioned hardenability copolymerization resin, and the hardening resin which it increases until now also, and is high sensitivity, and cannot cause viscosity increase easily.

[0022]The third purpose of this invention is to provide the method of raising transparency with the sensitivity of the above-mentioned hardenability copolymerization resin, and the hardening resin which it increases until now also, and is high sensitivity, and was excellent in transparency.

[0023]The fourth purpose of this invention is to provide the hardenability resin composition containing the improved above-mentioned hardening resin of high sensitivity.

[0024]The fifth purpose of this invention is to provide the light filter and liquid crystal panel which formed the columnar spacer of the coloring layer, the protective film, and/or the cell gap using the improved above-mentioned hardenability resin composition.

[0025]

[Means for Solving the Problem]High sensitivity hardening resin provided in this invention, It has a main chain which consists of a constitutional unit which has an acidic functional group at least, and a constitutional unit which has a hydroxyl group, A radical polymerization nature group content isocyanate compound consists of a polymer which said acidic functional group carries out an amide bond in part at least via an isocyanate group of the isocyanate compound concerned, and is carrying out the urethane bond of/or said hydroxyl group in part at least, A charge of said radical polymerization nature group content isocyanate compound converts into equivalent ratio (NCO/OH) of said isocyanate group to a hydroxyl group of said main chain, and is characterized by being 1.0 or more.

[0026]By adjusting a charge of a radical polymerization nature group content isocyanate compound so that said equivalent ratio (NCO/OH) may become 1.0 or more, it can become possible to introduce a side chain of a radical polymerization nature group by a high ratio into

hardening resin, and sensitivity of hardening resin can be raised.Since the high sensitivity hardening resin of this invention can adjust content of a constitutional unit which has an acidic functional group in proper proportion, it can adjust alkali solubility (development nature) freely.

[0027]The above-mentioned equivalent ratio (NCO/OH) of an isocyanate group is adjusted or more to 1.0, and it is preferred to make with a charge a content ratio of a constitutional unit which has a hydroxyl group more than 14 mol %. By making a charge of a constitutional unit which an introduction rate of an isocyanate group is raised and has a hydroxyl group simultaneously by adjusting the above-mentioned equivalent ratio (NCO/OH) of an isocyanate group or more to 1.0 more than 14 mol %, Since a portion to which an isocyanate group reacts increases, it becomes possible to introduce a side chain of a radical polymerization nature group into a photoresist polymer very so much, and high sensitivity is obtained especially.

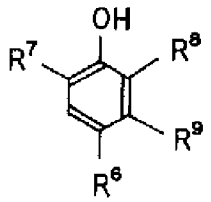
[0028]As for a maximum of a charge of a radical polymerization nature group content isocyanate compound, it is preferred to adjust so that the above-mentioned equivalent ratio (NCO/OH) of an isocyanate group may become 2.0 or less. When the above-mentioned equivalent ratio (NCO/OH) is 2.0 or more, into hardening resin, an unreacted radical polymerization nature group content isocyanate compound remains so much, and the physical properties of the hardening resin concerned are reduced.

[0029]An unreacted radical polymerization nature group content isocyanate compound is also usually mixed in hardening resin of this invention. Quantity of a radical polymerization nature group content isocyanate compound actually introduced into a photoresist polymer which is an essential ingredient of hardening resin as a side chain can be measured by ^{1}H-NMR. After a polystyrene equivalent weight average molecular weight removes 5000 or less ingredient from hardening resin of this invention by methods, such as reprecipitation refining, If a double bond of a radical polymerization nature group content isocyanate compound introduced into a photoresist polymer of the amount fractionation of polymers is measured by ^{1}H-NMR, quantity of residue of a radical polymerization nature group content isocyanate compound to 100 mol of constitutional units of a main chain will amount to 8 mol or more.

[0030]In this invention, a manufacturing method of high sensitivity hardening resin, To a raw material polymer which has a main chain which consists of a constitutional unit which has an acidic functional group at least, and a constitutional unit which has a hydroxyl group. A radical polymerization nature group content isocyanate compound is converted into equivalent ratio (NCO/OH) of an isocyanate group to a hydroxyl group of said main chain, and is made to react at 1.0 or more rate.

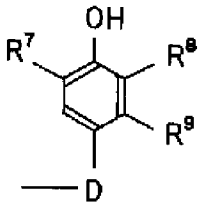
[0031]The aforementioned radical polymerization nature group content isocyanate compound is made to trickle and react to a solution which made a solvent dissolve or distribute the aforementioned raw material polymer in one mode of the above-mentioned manufacturing method. In making a radical polymerization nature group content isocyanate compound dropped little by little into a solution of a raw material polymer (dropping test), Even if equivalent ratio (NCO/OH) of an isocyanate group to conditions with comparatively few charges of a radical polymerization nature group content isocyanate compound, i.e., a hydroxyl group, is the conditions of the 1.0 neighborhoods, hardening

resin of high sensitivity is easy to be obtained.
[0032]To a raw material polymer which has a main chain which consists of a constitutional unit which has an acidic functional group at least, and a constitutional unit which has a hydroxyl group in this invention. After making a radical polymerization nature group content isocyanate compound react and compounding high sensitivity hardening resin, the stability of high sensitivity resin can be raised by making alcohol react further. An alcoholic processing body of high sensitivity resin is conjectured that alcohol has the molecular structure which an acidic functional group of a main chain of high sensitivity resin combined in part at least via a hydroxyl group of the alcohol concerned. Since it will become difficult to produce a viscosity rise if alcoholic processing of the high sensitivity resin is carried out, preservability improves, and control of coating becomes easy, and it becomes difficult to produce coating nonuniformity.
[0033]In this invention, when forming a principal chain part of a raw material polymer for hardening resin, i.e., a photoresist polymer, it is preferred to use a non-nitrile system azo polymerization initiator or a peroxide system polymerization initiator as a polymerization initiator, and to perform a polymerization reaction. When making a radical polymerization nature group content isocyanate compound react to a raw material polymer, it is preferred to use a compound chosen from phosphite system compounds expressed with a phenol system compound and a following formula (15) which are expressed with a following formula (9) as polymerization inhibitor. When high sensitivity hardening resin is formed using the above-mentioned specific polymerization initiator and/or the above-mentioned specific polymerization inhibitor, obtained reaction mixture shows high light transmission in a visible region and an ultraviolet region. Therefore, since there are few coloring components, a coat excellent in transparency can be formed, and even if it uses as coating liquid as it is, since light transmission in an ultraviolet region is also high, it excels in exposure sensitivity, without refining reaction mixture containing high sensitivity hardening resin.
[0034]
[Formula 16]
式(9)



(The inside of a formula and R^6 are hydrogen, an alkyl group of the carbon numbers 1-5, or a following formula (10).)
[Formula 17]

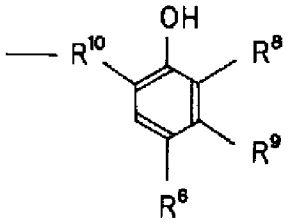
式 (10)



D in an example and a formula (10) shows the alkylene group of -S- and the carbon numbers 1-10, or the alkylidene group of the carbon numbers 1-10.R^7 shows hydrogen or the alkyl group of the carbon numbers 1-10. R^8 is hydrogen, an alkyl group of the carbon numbers 1-10, or a following formula (11).

[Formula 18]

式 (11)

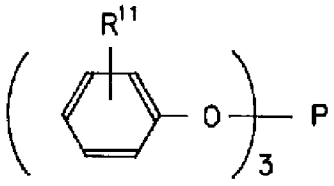


R^{10} in an example and a formula (11) shows an alkylene group of the carbon numbers 1-10, or an alkylidene group of the carbon numbers 1-10. R^9 shows hydrogen or an alkyl group of the carbon numbers 1-10. However, one is an alkyl group of R^7 and the R^8 which is a tert-butyl group or for which it has a cyclohexyl group at least. A substituent of identical codes may be mutually the same, or may differ.

[0035]

[Formula 19]

式 (15)



[0036](R^{11} shows hydrogen or the alkyl group of the carbon numbers 1-20 among a formula.))

[0037]By using the above-mentioned specific polymerization initiator and/or the above-mentioned specific polymerization inhibitor, For example. [whether the reaction mixture containing high sensitivity hardening resin is diluted with acetic acid-3-methoxy butyl as it is, and] Or the high sensitivity hardening resin separated from reaction mixture is dissolved by acetic acid-3-methoxy butyl, When 20wt% of an acetic acid-3-methoxy butyl solution is prepared as resin solid content and this

prepared solution is put into the quartz cell of 1-cm drawing, the light transmission at 400 nm of a visible region shows not less than 60%, or the light transmission at 360 nm of an ultraviolet region shows not less than 50%.

[0038]A hardenability resin composition provided in this invention contains the above-mentioned high sensitivity hardening resin as an essential ingredient. A hardenability resin composition of this invention has inherited character which was excellent in high sensitivity hardening resin as an essential ingredient as it is. That is, since it can be made to harden to inside of a short time with a small light exposure, the productivity of coat formation is high. Since a viscosity rise cannot break out easily due to alcoholic processing of high sensitivity hardening resin, it excels also in preservability or the control nature of coating, and a coat of uniform thickness and a pattern of exact size and shape are obtained. It is possible to form a coat of which it excels also in transparency and transparency is required.

[0039]According to this invention, after exposing a coating film which applied the aforementioned hardenability resin composition on a substrate, prebaked it, and formed it, thickness (front [development] thickness) is measured, After developing and carrying out postbake of the exposed coating film, thickness (thickness after the last hardening) is measured again, A remaining rate of membrane is measured according to following formula remaining-rate-of-membrane (%) =(front [after / the last hardening / thickness (micrometer) / development] thickness (micrometer)) x100, On the other hand, the same hardenability resin composition is applied on a substrate on the same conditions as measuring a remaining rate of membrane, Since a prebaked coating film is thoroughly stiffened by exposure, thickness (full exposure thickness) is measured, After carrying out postbake on the same conditions as a developing process omitting an exposed coating film and measuring a remaining rate of membrane, thickness (the last thickness without a developing process) is measured again, A reference remaining rate of membrane is measured according to following formula reference remaining-rate-of-membrane (%) =(last thickness (micrometer) / full exposure thickness without developing process (micrometer)) x100, When a computed remaining rate of membrane determines the smallest light exposure that becomes equal to a reference remaining rate of membrane as 1% of an error span as the minimum light exposure, it is possible for that the minimum light exposure concerned is below 100 mJ/cm^2 to obtain a hardenability resin composition of high sensitivity very much.

[0040]Thus, a hardenability resin composition of this invention obtained, It is suitable for forming a columnar spacer for maintaining a protective film which covers a coloring layer of a light filter, and the coloring layer concerned, and a cell gap of a liquid crystal panel, and a columnar spacer of a coloring layer of desired thickness, a protective film, and desired height can be formed with sufficient accuracy.

[0041]

[Embodiment of the Invention]The high sensitivity hardening resin provided by this invention, It has a main chain which consists of a constitutional unit which has an acidic functional group at least, and a constitutional unit which has a hydroxyl group, It consists of a photoresist polymer combined when [of the acidic functional group contained in these constitutional units, or a hydroxyl group] the isocyanate group of the isocyanate compound concerned reacts in part at

least in a radical polymerization nature group content isocyanate compound.

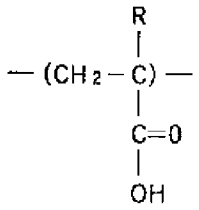
[0042]The constitutional unit which has an acidic functional group is an ingredient which contributes to alkali development property, and the content ratio is adjusted with the grade of the alkali solubility required of hardening resin. As a monomer used in order to introduce the constitutional unit which has an acidic functional group to the main chain of a polymer, the compound which has a double bond content group and an acidic functional group can be used. Although an acidic functional group is usually a carboxyl group, as long as it is an ingredient which can contribute to alkali development property, the thing besides carboxyl Motomochi may be sufficient as it.

[0043]As a constitutional unit which has an acidic functional group, the constitutional unit expressed with a following formula (1) is preferred.

[0044]

[Formula 20]

式 (1)



[0045](R shows hydrogen or the alkyl group of the carbon numbers 1-5 among a formula.)

[0046]R contained in a formula (1) and other formulas mentioned later is hydrogen or an alkyl group of the carbon numbers 1-5. As an alkyl group, a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, n-pentyl group, etc. are illustrated. As a monomer used in order to introduce the constitutional unit of a formula (1), PUTEN etc. are illustrated to acrylic acid, methacrylic acid, 2-carboxy-1-butene, 2-carboxy-1-pentene, 2-carboxy-1-hexene, and 2-carboxy-1-.

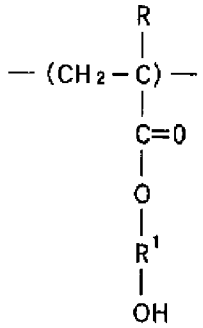
[0047]The constitutional unit which has a hydroxyl group is an ingredient into which a radical polymerization nature group is introduced fundamentally. That is, although some radical polymerization nature group content isocyanate compounds added to the system of reaction react to the acidic functional group of a main chain and it forms the side chain of a radical polymerization nature group, most isocyanate compounds concerned react to the hydroxyl group of a main chain, and it forms the side chain of a radical polymerization nature group. Therefore, the joint-right rate of a constitutional unit of having a hydroxyl group is prepared by the grade of photopolymerization nature required of hardening resin. As a monomer used in order to introduce the constitutional unit which has a hydroxyl group to the main chain of a polymer, the compound which has a double bond content group and a hydroxyl group can be used.

[0048]As a constitutional unit which has a hydroxyl group, a constitutional unit expressed with a following formula (2) is preferred.

[0049]

[Formula 21]

式 (2)



[0050](R is the same as the above among a formula, and R^1 shows the alkylene group of the carbon numbers 2-4.)

[0051]R^1 contained in a formula (2) is an alkylene group of the carbon numbers 2-4, for example, can illustrate ethylene, a propylene group, a butylene group, etc. As a monomer used in order to introduce the constitutional unit of a formula (2), 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 4-hydroxy butyl acrylate, 4-hydroxybutyl methacrylate, etc. are illustrated.

[0052]Although the main chain of a photoresist polymer contains a constitutional unit like the formula (1) which has an acidic functional group, and a constitutional unit like the formula (2) which has a hydroxyl group as an indispensable copolymerization ingredient, it may contain other copolymerization ingredients. For example, in the main chain, the constitutional unit which has an aromatic carbon ring, and/or the constitutional unit which has an ester group may contain.

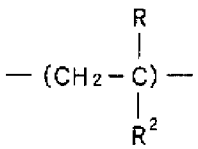
[0053]When a constitutional unit which has an aromatic carbon ring makes hardening resin coat formation, such as a protective film of a light filter, it is an ingredient which gives coat nature to the hardening resin concerned. As a monomer used in order to introduce a constitutional unit which has an aromatic carbon ring to a main chain of a polymer, a compound which has a double bond content group and an aromatic carbon ring can be used.

[0054]As a constitutional unit which has an aromatic carbon ring, a constitutional unit expressed with a following formula (3) is preferred.

[0055]

[Formula 22]

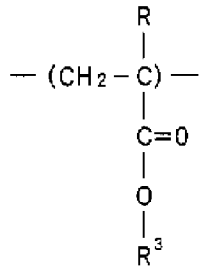
式 (3)



[0056](R is the same as the above among a formula, and R^2 shows an aromatic carbon ring.)

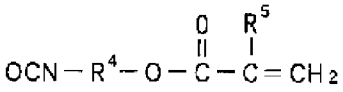
[0057]R^2 contained in a formula (3) is an aromatic carbon ring, for example, a phenyl group, a naphthyl group, etc. are illustrated. As a monomer used in order to introduce the constitutional unit of a formula (3), For example, styrene and alpha-methylstyrene can be illustrated and the aromatic ring may be replaced by amino groups, such as alkyl groups, such as halogen atoms, such as chlorine and bromine, a methyl group, and an ethyl group, an amino group, and a dialkylamino group, the cyano group, the carboxyl group, the sulfonic acid group, the phosphoric acid machine, etc.

[0058]A constitutional unit which has an ester group is an ingredient which controls the alkali development property of hardening resin. As a monomer used in order to introduce a constitutional unit which has an ester group to a main chain of a polymer, a compound which has a double bond content group and an ester group can be used.
[0059]As a constitutional unit which has an ester group, a constitutional unit expressed with a following formula (4) is preferred.
[0060]
[Formula 23]
式 (4)



[0061](R is the same as the above among a formula, and R^3 shows an alkyl group or an aralkyl group.)
[0062]R^3 contained in a formula (4) is an alkyl group or an aralkyl group, for example, aralkyl groups, such as an alkyl group of the carbon numbers 1-12, benzyl, and a phenylethyl group, are illustrated. As a monomer used in order to introduce the constitutional unit of a formula (4), For example, methyl acrylate (meta), ethyl acrylate (meta), butyl acrylate (meta), (Meta) Acrylic acid-2-ethylhexyl, acrylic acid (meta) phenyl, (Meta) Acrylic acid cyclohexyl, acrylic acid (meta) dicyclopentanil, (Meta) The ester species of acrylic acid (meta), such as acrylic acid dicyclopentanil oxyethyl, acrylic acid (meta) iso BONIRU, acrylic acid (meta) benzyl, and acrylic acid (meta) phenylethyl, is illustrated.
[0063]For every constitutional unit, a monomer used in order to introduce a constitutional unit of a formula (1) - a formula (4) to a main chain of a photoresist polymer may be independent, or what was illustrated, respectively may be used for it for two or more sorts, mixing.
[0064]Said acidic functional group carries out [a radical polymerization nature group content isocyanate compound] an amide bond to a main chain which comprises each of above-mentioned constitutional units in part at least via an isocyanate group of the isocyanate compound concerned, And the urethane bond of/or said hydroxyl group is carried out in part at least, and a side chain of a radical polymerization nature group is formed.
[0065]A (meth)acryloyloxy alkyl isocyanate of a formula (5) can be used as a radical polymerization nature group content isocyanate compound. An acrylic (meta) means being either an acrylic group or an methacrylic group, and that as used in this invention means that acryloyl (meta) is either an acrylyl group or a methacryloyl group.
[0066]
[Formula 24]

式 (5)



[0067](R4 shows an alkylene group among each formula, and R5 shows hydrogen or methyl.)
[0068]In a (meth)acryloyloxy alkyl isocyanate of a formula (5), it is preferred to use what an acrylyl group (meta) combined with an isocyanate group (-NCO) via an alkylene group of the carbon numbers 2-6. Specifically, 2-acryloyloxyethyl isocyanate, a 2-methacryloyl ethylisocyanate, etc. are illustrated. A 2-methacryloyl ethylisocyanate is marketed with trade names, such as "currant MOI" by Showa Denko K. K. etc., for example.
[0069]In hardening resin of this invention, when content of each constitutional unit of a main chain is expressed with a rate of a charge when the amount of the total used of a monomer for forming a main chain and a radical polymerization nature group content isocyanate compound (the total charge) is made into the whole quantity, it is as follows.
[0070]first -- being adjusted in order to respond to a grade of alkali solubility required as having mentioned above a content ratio of a constitutional unit like a formula (1) which has an acidic functional group -- a charge -- a table -- the bottom -- the time -- usually -- 5-mol % - 55-mol % -- it may be 10-mol % - 30-mol % preferably.
[0071]a content ratio of a constitutional unit like a formula (2) which has a hydroxyl group is adjusted so that it may respond to a grade (sensitivity) of photopolymerization nature demanded -- a charge -- a table -- the bottom -- the time -- usually -- 5-mol % - 95-mol % -- it may be 14-mol % - 50-mol % preferably. Though an introduction rate of a radical polymerization nature group to quantity of a hydroxyl group is high when there are too few these constitutional units since a constitutional unit which has a hydroxyl group is a portion which introduces a radical polymerization nature group, content of a radical polymerization nature group to the whole hardening resin becomes low, and high sensitivity is not obtained. On the other hand, since it becomes difficult to melt into an organic solvent when there are too many constitutional units which have a hydroxyl group, composition of hardening resin becomes difficult.
[0072]in order that a content ratio of a constitutional unit like a formula (3) which has an aromatic carbon ring may adjust coat nature -- a charge -- a table -- the bottom -- the time -- usually -- 0-mol % - 75-mol % -- it may be 5-mol % - 50-mol % preferably.
[0073]in order that a content ratio of a constitutional unit like a formula (4) which has an ester group may control alkali development property if needed -- a charge -- a table -- the bottom -- the time -- usually -- 0-mol % - 75-mol % -- it may be 5-mol % - 50-mol % preferably.
[0074]In this invention, a charge of a radical polymerization nature group content isocyanate compound is important especially in order to raise sensitivity of hardening resin. In this invention, a charge of a radical polymerization nature group content isocyanate compound is converted into equivalent ratio (NCO/OH) of an isocyanate group to a hydroxyl

group which a main chain of a photoresist polymer has, and is adjusted by 1.0 (namely, more than equivalent weight) or more. Quantity of a hydroxyl group is computed from a charge of a constitutional unit specifically like a formula (2) which has a hydroxyl group, and quantity of an isocyanate group is computed from a charge of a radical polymerization nature group content isocyanate compound, and the above-mentioned equivalent ratio (NCO/OH) is drawn from these calculated values. By making this equivalent ratio (NCO/OH) or more into 1.2 preferably 1.0 or more, it can become possible to introduce a side chain of a radical polymerization nature group by a high ratio, and sensitivity of hardening resin can be raised.

[0075]The above-mentioned equivalent ratio (NCO/OH) of an isocyanate group is adjusted or more to 1.0, and it is preferred to make with a charge a content ratio of a constitutional unit like a formula (2) which has a hydroxyl group more than 14 mol %. By making a charge of a constitutional unit which an introduction rate of an isocyanate group is raised and has a hydroxyl group simultaneously by adjusting the above-mentioned equivalent ratio (NCO/OH) of an isocyanate group or more to 1.0 more than 14 mol %, Since a portion to which an isocyanate group reacts increases, it becomes possible to introduce a side chain of a radical polymerization nature group into a photoresist polymer very so much, and high sensitivity is obtained especially.

[0076]As for a maximum of a charge of a radical polymerization nature group content isocyanate compound, it is preferred to adjust so that the above-mentioned equivalent ratio (NCO/OH) of an isocyanate group may become 2.0 or less. When the above-mentioned equivalent ratio (NCO/OH) exceeds 2.0, into hardening resin, an unreacted radical polymerization nature group content isocyanate compound remains so much, and the physical properties of a coat formed using the hardening resin concerned are reduced. In order to prevent thickening of hardening resin, in performing the alcoholic below-mentioned processing, an isocyanate group of a radical polymerization nature group content isocyanate compound which remains while it has been unreacted in hardening resin reacts to alcohol, and it disappears, but a portion of a radical polymerization nature group remains even in such a case. As a result, into hardening resin, a monofunctional monomer will remain so much and reduces sensitivity of hardening resin.

[0077]In order to manufacture hardening resin which consists of the above-mentioned photoresist polymer, First, a constitutional unit like a formula (1) which has an acidic functional group at least, Consist of a constitutional unit like a formula (2) which has a hydroxyl group, and if needed further. What is necessary is to manufacture a polymer (raw material polymer) which has a main chain containing a constitutional unit like a formula (3) which has an aromatic carbon ring, a constitutional unit like a formula (4) which has an ester group, or other constitutional units, and just to make a radical polymerization nature group content isocyanate compound react.

[0078]As a solvent for a polymerization used in order to manufacture a raw material polymer, A solvent which it does not have active hydrogen, such as a hydroxyl group and an amino group, preferably. For example, ether, such as a tetrahydrofuran; Diethylene glycol dimethyl ether, Glycol ether, such as diethylene-glycol diethylether and diethylene-glycol methyl ethyl ether. Cellosolve ester species, such as methyl-cellosolve acetate, propylene-glycol-monomethyl-ether acetate, acetic acid-3-methoxy butyl, etc. are mentioned, and aromatic hydrocarbon,

ketone, ester species, etc. can be used.
[0079]As a polymerization initiator used in order to manufacture a raw material polymer, what is generally known as a radical polymerization initiator can be used. As the example, 2,2'-azobisisobutyronitrile, 2, and 2'-azobis (2,4-dimethylvaleronitrile), Nitrile system azo compounds, such as 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) (nitrile system azo polymerization initiator); The dimethyl 2, 2'-azobis (2-methylpropionate), Non-nitrile system azo compounds, such as 2,2'-azobis (2,4,4-trimethyl pentane) (non-nitrile system azo polymerization initiator); t-hexylperoxy pivalate, tert-butylperoxy pivalate, 3 and 5, 5-trimethylhexanoylperoxide, Octanoylperoxide, lauroyl peroxide, stearoyl peroxide, 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate, SAKUSHI nick peroxide, 2,5-dimethyl- 2,5-JI (2-ethylhexanoyl peroxy) hexane, 1-cyclohexyl-1-methylethyl peroxy 2-ethylhexanoate, t-hexylperoxy 2-ethylhexanoate, 4-methylbenzoyl peroxide, benzoyl peroxide, Organic peroxide [, such as 1,1'-bis-(tert-butylperoxy) cyclohexane,] (peroxide system polymerization initiator); and hydrogen peroxide are mentioned. When using a peroxide as a radical polymerization initiator, it may be used as a redox type polymerization initiator combining this and a reducing agent.
[0080]In manufacture of a raw material polymer, in order to adjust weight average molecular weight, a molecular weight modifier can be used, For example, halogenated hydrocarbon;n-hexyl mercaptan, such as chloroform and carbon tetrabromide, N-octyl mercaptan, n-dodecyl mercaptan, tert-dodecyl mercaptan, Mercaptans, such as thioglycolic acid; xantho gene; TAPINOREN, such as dimethyl xantho gene disulfide and diisopropyl xantho gene disulfide, a alpha-methylstyrene dimer, etc. are mentioned.
[0081]Raw material polymers may be any of a random copolymer and a block copolymer. In manufacturing a random copolymer, it can do [polymerizing each monomer illustrated by the above-mentioned formula (1) thru/or formula (4) and a composition which consists of catalysts by making it drop and ripe over 2 to 5 hours by 80-110 ** temperature conditions in a polymerization tank into which a solvent was put, or].
[0082]A polystyrene equivalent weight average molecular weight of a raw material polymer which has a constitutional unit of a formula (1) - a formula (4). (it is only hereafter called "weight average molecular weight" or "Mw".) -- it is preferred that are considered as a thing of the range of 10,000-1,000,000, and acid value is made into 5 mgKOH/g - 400 mgKOH/g, and a hydroxyl value is made into a thing of 5 mgKOH/g - 400 mgKOH/g.
[0083]A reaction of raw material ****** and a radical polymerization nature group content isocyanate compound, After throwing in a radical polymerization nature group content isocyanate compound for the whole quantity at once in a solution of a raw material polymer under existence of a small amount of catalysts, it can carry out by continuing a fixed time reaction or being dropped little by little. Lauric acid dibutyl tin etc. are mentioned as a catalyst, and polymerization inhibitor, such as p-methoxy phenol, hydroquinone, naphthylamine, tert-butylcatechol, and 2,3-di-tert-butyl p-cresol, is used if needed.
[0084]In the case of a reaction, in making a radical polymerization nature group content isocyanate compound dropped little by little into a solution of a raw material polymer (dropping test), Even if equivalent ratio (NCO/OH) of an isocyanate group to conditions with comparatively few

charges of a radical polymerization nature group content isocyanate compound, i.e., a hydroxyl group, is the conditions of the 1.0 neighborhoods, hardening resin of high sensitivity is easy to be obtained. It is surmised that the reason is because the isocyanate group concerned reacts preferentially to a hydroxyl group and an unnecessary side reaction cannot occur easily when an isocyanate group always does not exist in small quantities in the system of reaction.

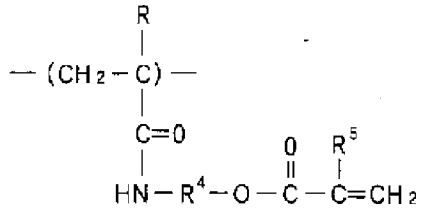
[0085]On the other hand, after throwing in a radical polymerization nature group content isocyanate compound for the whole quantity at once in a solution of a raw material polymer, in continuing a fixed time reaction (batch loading method), a way which uses a charge of a radical polymerization nature group content isocyanate compound as many eyes a little rather than a case where it is based on a dropping test, Hardening resin of high sensitivity is easy to be obtained. Therefore, in the case of a batch loading method, it is preferred to convert a charge of a radical polymerization nature group content isocyanate compound into equivalent ratio (NCO/OH) of an isocyanate group to a hydroxyl group which a main chain of a photoresist polymer has, and to adjust it or more to 1.2.

[0086]The amide bond of the radical polymerization nature group content isocyanate compound is carried out via an isocyanate to an acidic functional group in a raw material polymer. For example, the part emits carbon dioxide, it combines with a constitutional unit of a formula (1) by an amide bond, and a constitutional unit which is expressed with a following formula (6) is formed. On the other hand, to a hydroxyl group in a raw material polymer, the urethane bond of the radical polymerization nature group content isocyanate compound is carried out via an isocyanate. For example, an addition reaction is carried out to a constitutional unit of a formula (2), it combines with it by a urethane bond, and a constitutional unit which is expressed with a constitutional unit of a following formula (7) is formed.

[0087]

[Formula 25]

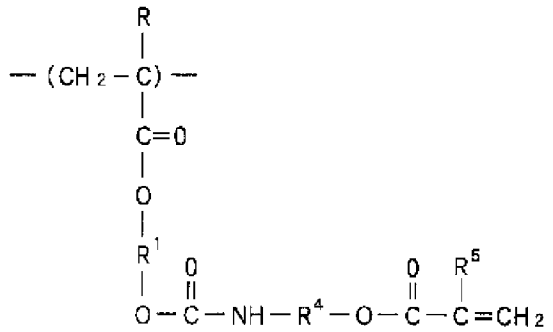
式 (6)



[0088]

[Formula 26]

式 (7)



[0089]Thus, the photoresist polymer in the hardening resin obtained, A constitutional unit like the formula (1) which has an acidic functional

group, and a constitutional unit like the formula (2) which has a hydroxyl group, It has the molecular structure which a constitutional unit like the formula (6) by which the radical polymerization nature group was introduced into the constitutional unit which has an acidic functional group, and a constitutional unit like the formula (7) by which the radical polymerization nature group was introduced into the constitutional unit of the formula (2) which has a hydroxyl group connected with arbitrary order.

[0090]A reaction of a radical polymerization nature group content isocyanate compound and a hydroxyl group has about 20-time reaction velocity as compared with a reaction with isocyanate compound concerned and an acidic functional group, especially a carboxyl group. Therefore, in a constitutional unit which a radical polymerization nature group is mainly introduced into a constitutional unit which has a hydroxyl group, and has an acidic functional group, though a radical polymerization nature group is introduced into a part of the acidic functional group, almost all acidic functional groups remain.

[0091]In using in order to form a columnar spacer for maintaining a cell gap of a protective film which covers a coloring layer of a light filter, and the coloring layer concerned for this hardening resin, or a liquid crystal panel, It is preferred 10,000-1,000,000, and that a polystyrene equivalent weight average molecular weight measured by GPC (gel permeation chromatography) adjusts in the range of 20,000-100,000 preferably. If weight average molecular weight is smaller than 10,000, even when development nature is too good, and cannot control pattern shape at the time of pattern exposure easily and a pattern can be produced, there are problems, like final thickness decreases (film decrease). On the other hand, when weight average molecular weight is larger than l, and 000 and 000, viscosity when it resist-izes becomes high too much, coating fitness falls, or development nature worsens, and there are problems, such as becoming difficult to escape from a pattern.

[0092]acid value of hardening resin -- 5mgKOH/g- it is preferred preferably to consider it as 10 mgKOH/g - 200 mgKOH/g 400 mgKOH/g. Acid value is related to alkali development property, and there are if development nature is bad when acid value is too low, problems, like adhesion to a substrate and light filter resin top is scarce. On the other hand, when acid value is too high, development nature is too good and there is a problem of being hard to control pattern shape at the time of pattern exposure. In hardening resin, a hydroxyl value can be adjusted in the range of 0 mgKOH/g - 200 mgKOH/g. Although it is not necessary to necessarily leave it, a hydroxyl group in a main chain of hardening resin is effective in adjusting solubility over a solvent, when leaving this.

[0093]What is shown below also in high sensitivity hardening resin obtained by this invention is preferred especially in order to form a columnar spacer for maintaining a cell gap of a protective film which covers a coloring layer of a light filter, and the coloring layer concerned, or a liquid crystal panel. Namely, it is based on the whole quantity of each constitutional unit which constitutes a main chain and a side chain of hardening resin, A charge of a constitutional unit in which a charge of a constitutional unit which has an acidic functional group has 10-30-mol % and a hydroxyl group More than 14 mol %. And a thing whose acid value a charge of a radical polymerization nature group content isocyanate compound is more than 14 mol %, and is 80 - 140 mgKOH/g and whose polystyrene equivalent weight average molecular weights are 10,000-100,000 is preferred. However, also in this case, a charge of a

radical polymerization nature group content isocyanate compound is converted into equivalent ratio (NCO/OH) of an isocyanate group to a hydroxyl group of a main chain, and is preferably adjusted by 1.2 or more 1.0 or more. As for a main chain of hardening resin, it is preferred to be constituted by constitutional unit of a formula (1) mentioned above, a formula (2), a formula (3), and a formula (4).

[0094]A still more desirable thing also in the above-mentioned hardening resin of illustration, It is based on the whole quantity of each constitutional unit which constitutes a main chain and a side chain of high sensitivity hardening resin, A charge of a constitutional unit in which a charge of a constitutional unit which has an acidic functional group has 10-30-mol % and a hydroxyl group 15-19-mol %, And a charge of a radical polymerization nature group content isocyanate compound is 18-26-mol %, and acid value is 90 - 120 mgKOH/g, and a polystyrene equivalent weight average molecular weight is a thing of 30,000-60,000.

[0095]An unreacted radical polymerization nature group content isocyanate compound is also usually mixed in high sensitivity hardening resin obtained by this invention. Quantity of a radical polymerization nature group content isocyanate compound actually introduced into a photoresist polymer which is an essential ingredient of hardening resin as a side chain can be measured by ^{1}H-NMR. After a polystyrene equivalent weight average molecular weight removes 5000 or less ingredient by suitable methods, such as reprecipitation refining, hardening resin obtained by this invention, If a double bond of a radical polymerization nature group content isocyanate compound introduced into a photoresist polymer of the amount fractionation of polymers is measured by ^{1}H-NMR, Quantity of residue of a radical polymerization nature group content isocyanate compound to 100 mol of constitutional units of a main chain amounts to 8 mol or more, and it reaches more than 12 mol % in an especially high thing of sensitivity.

[0096]for performing reprecipitation refining -- a solution (solid content: -- about 25 wt(s)%.) of for example, high sensitivity hardening resin Solvent: What is necessary is to dilute acetic acid-3-methoxy butyl with a tetrahydrofuran, to drop the diluent into isopropyl alcohol, hexane, or both partially aromatic solvent (isopropyl alcohol: hexane (weight ratio) =100:0-0:100), and just to collect depositing solids. Reaction mixture produced by making a radical polymerization nature group content isocyanate compound react to a raw material polymer may be diluted with a tetrahydrofuran as it is, and may be used for a reprecipitation process. A depositing solid is again dissolved by acetic acid-3-methoxy butyl, isopropyl alcohol of whether it is the same as last time and a different ratio and/or hexane may be independent, or a diluent obtained by diluting with a tetrahydrofuran may be dropped into a partially aromatic solvent, and depositing solids may be collected. Thus, a molecular weight can remove 5000 or less ingredient from hardening resin by repeating a reprecipitation process several times 1 time or if needed.

[0097]When forming a protective film which covers a coloring layer or the coloring layer concerned of a light filter using high sensitivity hardening resin of this invention, high transparency is searched for from hardening resin. When you need high hardening resin of transparency, A monomer which has a double bond content group and an acidic functional group, and a monomer which has a double bond content group and a hydroxyl group, When making other monomers react if needed

furthermore and forming a principal chain part of a raw material polymer for hardening resin, i.e., a photoresist polymer, it is preferred to use a non-nitrile system azo polymerization initiator or a peroxide system polymerization initiator, and to perform a polymerization reaction. What was mentioned above can be used as a polymerization initiator of non-nitrile system azo or a peroxide system.

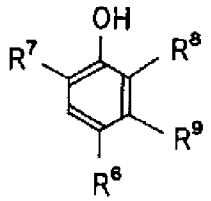
[0098]When making a radical polymerization nature group content isocyanate compound react to a raw material polymer, the transparency of hardening resin can be raised also by using a specific phenol system compound or a specific phosphite system compound as polymerization inhibitor.

[0099]That is, specific phenol system polymerization inhibitor which can raise the transparency of hardening resin can be expressed with a following formula (9).

[0100]

[Formula 27]

式 (9)

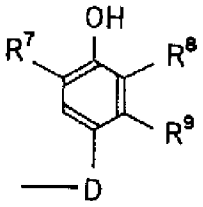


[0101](The inside of a formula and R^6 are hydrogen, an alkyl group of the carbon numbers 1-5, or a following formula (10).)

[0102]

[Formula 28]

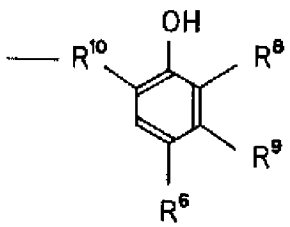
式 (10)



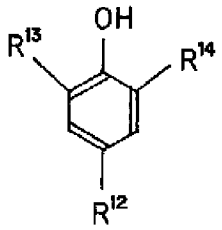
D in an example and a formula (10) shows the alkylene group of -S- and the carbon numbers 1-10, or the alkylidene group of the carbon numbers 1-10.R^7 shows hydrogen or the alkyl group of the carbon numbers 1-10. R^8 is hydrogen, an alkyl group of the carbon numbers 1-10, or a following formula (11).

[Formula 29]

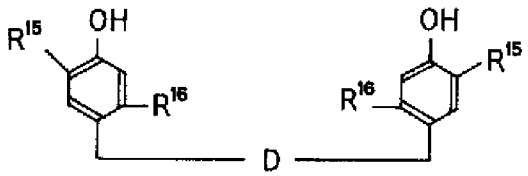
式 (11)



R^{10} in an example and a formula (11) shows the alkylene group of the carbon numbers 1-10, or the alkylidene group of the carbon numbers 1-10.R^{9} shows hydrogen or the alkyl group of the carbon numbers 1-10. However, one is an alkyl group of R^{7} and the R^{8} which is a tert-butyl group or for which it has a cyclohexyl group at least. The substituent of identical codes may be mutually the same, or may differ.
Also in the phenol system compound expressed with the above-mentioned formula (9), what is expressed with the following formula (12), (13), or (14) is preferred.
[0103]
[Formula 30]
式 (12)

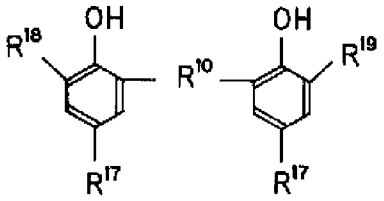


[0104](R^{12} shows hydrogen and an alkyl group of the carbon numbers 1-5 among a formula, and R^{13} and R^{14} show hydrogen or an alkyl group of the carbon numbers 1-10.) However, one is an alkyl group of R^{13} and the R^{14} which is a tert-butyl group or for which it has a cyclohexyl group at least.
3,5-di-tert-butyl-4-hydroxytoluene (BHT) can be mentioned as an example of a thing applicable to the above-mentioned formula (12).
[0105]
[Formula 31]
式 (13)



[0106](D shows the alkylene group of -S- and the carbon numbers 1-10, or the alkylidene group of the carbon numbers 1-10 among a formula, R^{15} shows hydrogen or the alkyl group of the carbon numbers 1-10, and R^{16} shows hydrogen or the alkyl group of the carbon numbers 1-10.) However, the substituent of identical codes may be mutually the same, or it may differ, and one is an alkyl group of the R^{15} which is a tert-butyl group or for which it has a cyclohexyl group at least.
[0107]As an example of a thing applicable to the above-mentioned formula (13), a 4,4'-thio-screw (3-methyl-6-tert-butylphenol) and a 4,4'-butylidene-screw (3-methyl-6-tert-butylphenol) can be mentioned.
[0108]
[Formula 32]

式 (14)



[0109](Among a formula, R^{10} shows the alkylene group of the carbon numbers 1-10, or the alkylidene group of the carbon numbers 1-10, R^{17} shows hydrogen or the alkyl group of the carbon numbers 1-5, and R^{18} and R^{19} show hydrogen or the alkyl group of the carbon numbers 1-10.) However, one is an alkyl group of R^{18} and the R^{19} which is a tert-butyl group or for which it has a cyclohexyl group at least. The substituent of identical codes may be mutually the same, or may differ.

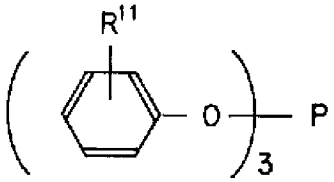
[0110]As an example of a thing applicable to the above-mentioned formula (14), A 2,2'-methylene-screw (4-methyl-6-tert-butylphenol), A 2,2'-methylene-screw (4-ethyl-6-tert-butylphenol) and 2,2'-dihydroxy-3,3'-JI (alpha-methyl-cyclohexyl)-5,5'-dimethyldiphenylmethane can be mentioned.

[0111]Specific phosphite system polymerization inhibitor which can raise the transparency of hardening resin can be expressed with a following formula (15).

[0112]

[Formula 33]

式 (15)



[0113](R^{11} shows hydrogen or the alkyl group of the carbon numbers 1-20 among a formula.))

[0114]Tris (nonyl-ized phenyl) phosphite can be mentioned as an example of the thing applicable to the above-mentioned formula (15).

[0115]The especially outstanding transparency is acquired by making a radical polymerization nature group content isocyanate compound react to the raw material polymer beforehand manufactured using the above-mentioned specific polymerization initiator using the above-mentioned specific polymerization inhibitor.

[0116]Since there is little coloring of obtained reaction mixture when hardening resin is compounded using the above-mentioned specific polymerization initiator and/or the above-mentioned specific polymerization inhibitor, a purification process for removing a coloring component from hardening resin can be simplified, or it can omit thoroughly. Therefore, it is also possible to use it as coating liquid for forming a pattern which can search for transparency like a coloring layer

of a light filter or a protective film as it is without refining reaction mixture containing hardening resin. For example. [whether reaction mixture containing high sensitivity hardening resin of this invention is diluted with acetic acid-3-methoxy butyl as it is, and] Or high sensitivity hardening resin separated from reaction mixture is dissolved by acetic acid-3-methoxy butyl, 20wt% of an acetic acid-3-methoxy butyl solution is prepared as resin solid content, and light transmission at 400 nm when this prepared solution is put into a quartz cell of 1-cm drawing shows outstanding transparency which will be not less than 70% preferably not less than 60%.

[0117]Although light transmission becomes low in near 480 nm and this kind of hardening resin has a tendency which shows a minimum point of light transmission, Hardening resin of transparency acquired by this invention does not show depression of such light transmission, but has the light transmission of not less than 90% preferably not less than 85% in near 480 nm under the above-mentioned measuring condition.

[0118]Hardening resin of transparency acquired by this invention, When high light transmission is shown in all the fields of visible light and it measures under the above-mentioned measuring condition, In 400 nm - 700 nm, not less than 60%, not less than 70% is shown preferably, in 450 nm - 700 nm, not less than 85% is shown preferably, and not less than 95% is preferably shown not less than 90% in 500-700 nm not less than 80%.

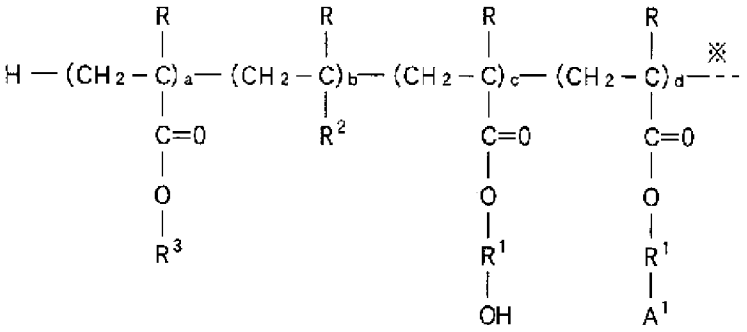
[0119]When hardening resin is compounded using the above-mentioned specific polymerization initiator and/or the above-mentioned specific polymerization inhibitor, obtained reaction mixture has little absorption also not only in a visible region but in an ultraviolet region. therefore, even when forming a coat, using reaction mixture containing this hardening resin as coating liquid as it is, a coat is deep, a until ultraviolet radiation line reaches, and exposure sensitivity improves. For example. [whether reaction mixture containing high sensitivity hardening resin of this invention is diluted with acetic acid-3-methoxy butyl as it is and] Or high sensitivity hardening resin separated from reaction mixture is dissolved by acetic acid-3-methoxy butyl, 20wt% of an acetic acid-3-methoxy butyl solution is prepared as resin solid content, and light transmission at 360 nm when this prepared solution is put into a quartz cell of 1-cm drawing shows outstanding diactinism which will be not less than 60% preferably not less than 50%. Since wavelength near 360 nm is also the effective wavelength of a photopolymerization initiator, when light transmission near [this] wavelength is high, an operation of a photopolymerization initiator is promoted and its exposure sensitivity improves further.

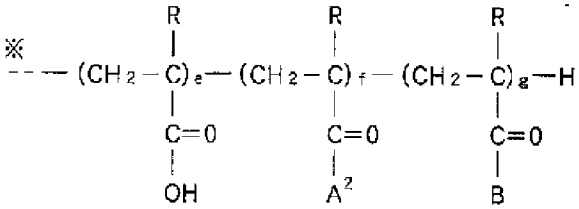
[0120]Since hardening resin of this invention has high sensitivity to exposure and alkali solubility and coating nature in resin can be adjusted suitably, It can use suitably as an active principle of photoresist, and is suitable for forming a columnar spacer for maintaining a cell gap of a coloring layer of a light filter, a protective film, or a liquid crystal panel especially.

[0121]However, if a solvent is made to dissolve or distribute this hardening resin, a molecular weight will increase even under a room temperature and viscosity will rise quickly. and when this hardening resin is mixed with an epoxy resin, an acrylic monomer, a polymerization initiator, etc., a solvent is dissolved or distributed and photoresist is prepared, a grade and speed of thickening are the much more -- it becomes remarkable.

[0122]Radical polymerization nature groups, such as an AKUROIRU (meta) group which exists in hardening resin, not only participate in a hardening reaction at the time of exposure, but considered at the beginning that this invention persons would also cause viscosity increase at the time of preservation. however, when a solution of the above-mentioned hardening resin was observed with a ^{1}H-NMR spectrum, even if viscosity of a solution rose, it was checked that the amount of double bonds of an AKUROIRU (meta-) group does not decrease. Therefore, a radical polymerization nature group did not cause viscosity increase.
[0123]Then, when a solution of the above-mentioned hardening resin was observed by FT-IR spectrum (infrared absorption spectrum), it was checked that a minute peak near 1800-cm^{-1} disappears with a rise of viscosity. A peak was observed by the too same position when FT-IR spectrum of an acrylic acid anhydride was observed in consideration of this audit observation. An acid anhydride was obtained when an AKURO (meta) yloxy ethylisocyanate was made to react to acrylic acid and acetic acid which has a carboxyl group similarly.
[0124]These results to the above-mentioned hardening resin is ******** when it has an acid anhydride group. A polymer which consists of a constitutional unit [like a formula (1) which has an acidic functional group at least] in which this acid anhydride group is, and a constitutional unit like a formula (2) which has a hydroxyl group, That is, when making a radical polymerization nature group content isocyanate compound react without a raw material polymer and manufacturing hardening resin, as a result of an isocyanate group's working as a dehydrator, when an acidic functional group which is mainly in the same intramolecular carries out dehydration condensation, it is surmised that it sub**. An acid anhydride group produced in a molecule of hardening resin, If a solvent is dissolved or distributed and the resin concerned is neglected, by reacting to a hydroxyl group contained in other chains of hardening resin, and carrying out an ester bond, the molecules of hardening resin will be made to construct a bridge and, as a result, it will be surmised that increase of a molecular weight and a rise of viscosity are caused.
[0125]Such a thickening phenomenon can be prevented by processing the above-mentioned hardening resin in alcohol. What is necessary is just to add alcohol, before viscosity of the solution concerned begins to rise in a solution which made a solvent dissolve or distribute the hardening resin concerned, or before a viscosity rise is completed in order to process hardening resin in alcohol. Each monomer is polymerized in synthetic solvents, such as MBA (acetic acid-3-methoxy butyl, $CH_3CH(OCH_3)CH_2CH_2OCOCH_3$), A radical polymerization nature group content isocyanate compound may be made to trickle and react to a solution of a raw material polymer obtained by compounding a raw material copolymer which consists of a constitutional unit which has an acidic functional group at least, and a constitutional unit which has a hydroxyl group, and alcohol may be succeedingly added to obtained reaction mixture. A reaction condition in particular at the time of addition is not restricted, and while reaction mixture is hot, it may add, or it may add at a room temperature, and even if it throws in alcohol at a stretch in reaction mixture, it does not interfere.
[0126]If an effective amount of alcohol of a more than is added in a solution of the above-mentioned hardening resin while an acid anhydride group is still unreacted, the alcohol concerned will compete with a hydroxyl group in a main chain of hardening resin, and will scramble for

an acid anhydride group, and it will be surmised that the acid anhydride group concerned is esterified. As a result, crosslinking reaction between molecules of hardening resin is prevented, and it is surmised that increase of a molecular weight and a rise of viscosity are prevented.
[0127]Hardening resin obtained by such alcoholic processing, It has a main chain which consists of a constitutional unit which has an acidic functional group at least, and a constitutional unit which has a hydroxyl group, Said acidic functional group carries out an amide bond in part at least via an isocyanate group of the isocyanate compound concerned, and an isocyanate compound is carrying out the urethane bond of/or said hydroxyl group in part at least, Alcohol is conjectured to have the molecular structure in which said acidic functional group carried out the ester bond in part at least via a hydroxyl group of the alcohol concerned.
[0128]Molecular structure of an alcoholic processing polymer produced by adding alcohol to hardening resin which has a main chain which consists of a constitutional unit of the above-mentioned formula (1), a formula (2), a formula (3), and a formula (4) as an example can be expressed with a following formula (8).
[0129]
[Formula 34]
式 (8)





[0130](Among a formula, R, R^1, R^2, and R^3 are the same as the above, and) The residue to which the radical polymerization nature group content isocyanate compound carried out the urethane bond of the A^1, the residue to which the radical polymerization nature group content isocyanate compound carried out the amide bond of the A^2, and B show the residue in which alcohol carried out the ester bond. a, b, and c show zero or more integers, and d, e, f, and g show one or more integers.

Random copolymerization of each constitutional unit may be carried out, or block copolymerization may be carried out.
[0131]While a part or all of acid anhydride groups has still been unreacted and remaining into a photoresist polymer, it is necessary to make it react to alcohol in this invention. For example, if it is immediately after making a radical polymerization nature group content isocyanate compound react to a raw material polymer which consists of a constitutional unit like a formula (1) which has an acidic functional group at least, and a constitutional unit like a formula (2) which has a hydroxyl group, and manufacturing hardening resin, Since an acid anhydride group does not react to a hydroxyl group at all yet and a viscosity rise has not started, it can react to alcohol added from the outside. If a viscosity rise is advancing and it has not ended thoroughly yet even if it is after neglecting a solution of hardening resin for a while under a room temperature, since an unreacted acid anhydride group remains, a certain grade can prevent a viscosity rise, and it is effective.
[0132]A kind in particular of alcohol used for inhibition of a thickening phenomenon is not limited, but as long as it is a compound which has an alcoholic hydroxyl group, it is usable and it may contain N, O, S, P, etc. Usually, it is comparatively easy to deal with a way of a thing of low molecular weight. for example, whether it is a with a carbon number of about one to 20 thing, and N, O, S, P, etc. are included and an included thing -- more specifically, Methanol, ethanol, propanol, butanol, a pentanol, Alcohols solvents, such as a hexanol, heptanol, octanol, and decanol; Methoxy alcohol, Cellosolve Solvents, such as ethoxyalcohol; Methoxyethoxy ethanol, Carbitol system solvents, such as ethoxyethoxyalcohol; Ethylene glycol monomethyl ether, Diethylene glycol monomethyl ether, ethylene glycol monopropyl ether, Ethers solvents, such as propylene glycol monomethyl ether; 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 2-hydroxybutyl (meta) acrylate, Unsaturated bond content solvents, such as a 4-penten-1-oar, tetramethylol METANTORI (meta) acrylate, TETORATORI methylol pro pantry (meta) acrylate, and dipentaerythritol hexaacrylate, etc. can be used.
[0133]Suitable means, such as reprecipitation refining, may remove unreacted alcohol which remains in a solution of hardening resin if needed. After adding alcohol in a solution of hardening resin, it may mix to a solvent for coating with other materials as it is, and may be considered as coating liquid, and alcohol may be evaporated with a solvent for coating in a drying process after carrying out coating of this. Like this example, when evaporating remains alcohol together with another solvent, the one where a difference of the boiling point of a solvent mixed with the boiling point of alcohol or a difference of a vapor rate of a solvent mixed with a vapor rate of alcohol is possible smaller is desirable, and a thing without a difference is ideal. The one where difference of the boiling point of alcohol and a solvent and difference of a vapor rate of alcohol and a solvent of both are smaller is preferred. A difference of the boiling point of a solvent mixed with the boiling point of alcohol from this viewpoint has a less than 75 ** preferred thing, and is preferred. [of especially a less than 40 ** thing] A difference of a vapor rate of the alcohol concerned and a vapor rate of a solvent for coating liquid is 90. A certain thing is preferred at [n-BuOAc=100], and it is 30. Especially a certain thing is preferred at [n-BuOAc=100]. It is preferred to fulfill conditions of the above [both boiling points and vapor rates of alcohol]. It is here and is a vapor rate (unit :). [n-BuOAc=100] a

ratio at the time of setting a vapor rate by a weight method of acetic acid normal butyl (n-BuOAc) at 25 ** to 100 -- it is expressed with a vapor rate.

[0134]Quantity of alcohol used for inhibition of a thickening phenomenon is suitably adjusted according to quantity of an acid anhydride group contained in hardening resin. Preferably, it is considered as about 10 to 120% of the weight of quantity of hardening resin.

[0135]In order to stop a viscosity rise of a solution of hardening resin thoroughly substantially, it is necessary for it to be necessary to carry out fixed time neglect of the reaction mixture, after adding alcohol, and to fully reduce quantity of an acid anhydride group, and to ripen an alcoholic processing polymer. Although reaction mixture may be allowed to stand at a room temperature, aging can be made to complete by heating for a short time. It is preferred to ripen reaction mixture which added alcohol by neglecting it during less than 72 hours at temperature of 30-170 **.

[0136]Here, if maturing time in 90 ** is shorter than 4 hours, resin cannot be stabilized thoroughly and an effect of thickening inhibition will fade, for example.

[0137]In manufacturing a resin composition of a photoresist using hardening resin of this invention, What is necessary is to dissolve in a resist solvent (solvent for coating for dilution), and just to make it distribute a photopolymerization nature monomer like a polyfunctional photopolymerization acrylate system monomer of two or more organic functions, a polymerization initiator, etc. with hardening resin which is main polymer.

[0138]A hardenability resin composition is made to usually contain hardening resin ten to 50% of the weight preferably five to 80% of the weight by a solid content ratio in this invention. If there is more content of hardening resin than 80 % of the weight, viscosity may become high too much, as a result, mobility may fall, and it may worsen at spreading nature. If there is less content of hardening resin than 5 % of the weight, viscosity becomes low too much, as a result, coat stability after spreading desiccation is insufficient, and problems, such as spoiling exposure and development fitness, may be produced.

[0139]As a polyfunctional acrylate system monomer contained as a photopolymerization nature monomer in a hardenability resin composition, For example, ethylene glycol (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, Propyleneglycol di(meth) acrylate, dipropylene GURIKORUJI (meta) acrylate, Poly ethylene glycol di (metha)acrylate, poly propyleneglycol di(meth) acrylate, HEKISANJI (meta) acrylate, neopentyl glycol di(metha)acrylate, GURISERINJI (meta) acrylate, GURISERINTORI (meta) acrylate, Glycerin tetra (meta) acrylate, TETORATORI methylol pro pantry (meta) acrylate, 1,4-butanediol diacrylate and pentaerythritol -- doria -- KURIRETO, trimethylolpropane triacrylate, pentaerythritol (meta-) acrylate, dipentaerythritol hexa (meta-) acrylate, etc. can be illustrated. These ingredients are independent or are used as a mixture.

[0140]As for a polyfunctional acrylate system monomer, it is preferred that at least one sort of monomers of three or more organic functions are included, and, as for the content, it is preferred to occupy about 30 to 95 % of the weight in a polyfunctional acrylate system monomer. To these polyfunctional acrylate system monomers. As a reaction diluent, methyl (meta) acrylate, ethyl (meta) acrylate, Monofunctional nature monomers, such as propyl (meta) acrylate, butyl (meta) acrylate, pentyl (meta)

acrylate, ethylhexyl (meta) acrylate, styrene, methylstyrene, and N-vinyl pyrrolidone, can be added.

[0141]content of a polyfunctional acrylate system monomer as a photopolymerization nature monomer -- the inside of a hardenability resin composition -- a solid content ratio -- it contains five to 40% of the weight preferably three to 50% of the weight. Adhesive strength of a film which will be formed if a polyfunctional acrylate system monomer will be less than 3% of the weight, Inconvenience that physical intensity becomes insufficient in some numbers, such as heat resistance, arises, and if this value exceeds 50 % of the weight, the stability of a hardenability resin composition will fall, and inconvenience that the flexibility of a film formed becomes insufficient arises. Also in order to raise dissolution property over a developing solution, this rate is required, in separating from the range of the amount of optimization, although carried out, a monomer cure rate becomes large, and pattern resolving produces SCUM and a mustache to the pattern circumference. Resist reattachment which comes from swelling and exfoliation partial when severe out of the further above-mentioned range arises, and exact pattern formation may be checked.

[0142]Furthermore, into a hardenability resin composition of this invention, a compound (epoxy resin) which has two or more epoxy groups in intramolecular can be blended if needed in order to aim at heat resistance, adhesion, and chemical-resistant (especially alkali resistance) improvement. As a compound which it has two or more pieces in intramolecular, an epoxy group, As a bisphenol A type epoxy resin, for example, Epicoat 1001, 1002, 1003, 1004, 1007, 1009, and 1010 (product made from oil recovery shell) etc.,As bisphenol F type epoxy resin, Epicoat 807 (product made from oil recovery shell) etc., As phenol novolak type epoxy resin, EPPN201, 202 (made by Nippon Kayaku), Epicoat 154 (product made from oil recovery shell) etc. can illustrate EOCN102, 103S, 104S, 1020, 1025 and 1027 (made by Nippon Kayaku), Epicoat 180S (product made from oil recovery shell), etc. as cresol novolak type epoxy resin. A cyclic aliphatic series epoxy resin and aliphatic series poly glycidyl ether can also be illustrated.

[0143]In these, a bisphenol A type epoxy resin, bisphenol F type epoxy resin, phenol novolak type epoxy resin, and cresol novolak type epoxy resin are preferred. Although many of compounds which have two or more of these epoxy groups in intramolecular are the amount objects of polymers, glycidyl ether of bisphenol A or the bisphenol F is a low molecular weight body, and such a low molecular weight body especially is preferred. An acrylic copolymer etc. which contain glycidyl (meta) acrylate, oxetane (meta) acrylate, alicyclic epoxy (meta) acrylate, etc. in a resin skeleton are effective.

[0144]In a hardenability resin composition, such an epoxy resin is a solid content ratio, and is usually contained five to 40% of the weight preferably zero to 60% of the weight. Content of an epoxy resin may be unable to give sufficient alkali resistance for a protective film in less than 5 % of the weight. On the other hand, if content of an epoxy resin exceeds 40 % of the weight, since the amount of epoxy resins with which photo-curing is not presented will increase too much and the preservation stability of a hardenability resin composition and development fitness will fall, it is not desirable. An epoxy resin is effective also in order to remove a tuck of a dry paint film of a hardenability resin composition, and sufficient effect reveals it with about 3 % of the weight of additions. An epoxy resin will react to an acidic group which remains in a coat

without reacting after exposure and alkaline development by heat-treatment, and alkali resistance excellent in a coat will be given.
[0145]A radical polymerization nature initiator can be used as a polymerization initiator. A radical polymerization nature initiator is a compound which generates a free radical, for example by energy of ultraviolet rays, Derivative; xanthone and thioxan ton derivatives, such as benzophenone derivatives, such as benzoin and benzophenone, or those ester; Chlorosulfonyl, A redox couple; organosulfur compound of halogen-containing compound; triazine; fluorenone; haloalkane; photoreduction nature coloring matter, such as chloromethyl polynuclear aromatic compounds, a chloromethyl heterocyclic compound, and chloromethyl benzophenones, and a reducing agent; there are a peroxide etc. Preferably IRGACURE 184, IRGACURE 369, IRGACURE 651, IRGACURE 907 (all are made in Tiba Specialty Chemicals), A ketone system, bi-imidazole compounds, etc., such as DAROKYUA (made by Merck Co.), ADEKA 1717 (made by Asahi Denka Kogyo K.K.), the 2,2'-bis(o-chlorophenyl)-4,5,4'-tetraphenyl- 1, and 2'-biimidazole (made in Kurogane Chemicals, Inc.), can be mentioned. These initiators can be used combining one sort or two sorts or more. When using two or more sorts together, it is good to make it not check the absorption spectral characteristic.
[0146]A radical polymerization nature initiator is usually preferably contained one to 15% of the weight 0.1 to 20% of the weight as a solid content ratio in a hardenability resin composition. If an addition of a radical polymerization nature initiator will be less than 0.1% of the weight, a photo-curing reaction will not progress, but there is a tendency for a remaining rate of membrane, heat resistance, chemical resistance, etc. to fall. If this addition exceeds 20 % of the weight, solubility to base resin will reach saturation, a crystal of an initiator deposits at the time of spin coating and coat leveling, and fault which it becomes impossible to hold the homogeneity of a film surface, and is called film roughness generating arises.
[0147]In preparing a hardenability resin composition, although it may add from the beginning to a resin composition which consists of said polyfunctional acrylate system monomer and hardening resin, when carrying out long term storage of the polymerization initiator comparatively, it is preferred [the polymerization initiator] to distribute or dissolve into a resin composition just before use.
[0148]A sensitizer may be added to expect improvement in photosensitivity. As a sensitizer to be used, a styryl system compound or a coumarin series compound is preferred. Specifically 2-(p-dimethylaminostyryl) quinoline, 2-(p-diethylaminostyryl) quinoline, 4-(p-dimethylaminostyryl) quinoline, 4-(p-diethylaminostyryl) quinoline, 2-(p-dimethylaminostyryl)-3,3-3H-Indore, 2-(p-diethylaminostyryl)-3,3-3H-Indore, 2-(p-dimethylaminostyryl) benzoxazole, 2 -(p-diethylaminostyryl)- Benzoxazole, 2-(p-dimethylaminostyryl) benzimidazole 2 -(p-diethylaminostyryl)- Benzimidazole etc. are mentioned.
[0149]As a coumarin series compound, a 7-diethylamino 4-methylcoumarin, A 7-ethylamino 4-trifluoromethyl coumarin, 4, a 6-diethylamino 7-ethylamino coumarin, 3-(2-benzimidazolyl)-7-N and N-diethylamino coumarin, 7-diethylamino cyclopenta(c) coumarin, a 7-amino-4-trifluoromethyl coumarin, 1,2,3,4,5,3 H,6 H,10H-tetrahydro 8-trifluoromethyl (1) benzo ******- (9,9 a,1-gh)-kino lysine 10-one, A 7-ethylamino 6-methyl-4-trifluoromethyl coumarin, 1,2,3,4,5,3 H,6 H,10H-

tetrahydro 9-cull BETOKISHI (1) benzo ******- (9,9 a,1-gh)-kino lysine 10-one, etc. are mentioned.

[0150]In an above-mentioned hardenability resin composition, various kinds of additive agents, for example, a surface-active agent, a silane coupling agent, etc. as shown at the following, can be added if needed.

[0151]A surface-active agent is blended in order to secure spreading fitness and film smooth nature after desiccation to a hardenability resin composition, For example, polyoxyethylene lauryl ether, polyoxyethylene stearylether, Polyoxyethylene alkyl ether, such as polyoxyethylene oleylether. Polyoxyethylene arylated alkyl ether, such as polyoxyethylene octylphenyl ether and polyoxyethylene nonylphenyl ether, Polyoxyethylene dialkyl ester, such as a polyoxyethylene JIRAU rate and polyoxyethylene distearate. The megger fuck F171, 172 and 173 (made by Dainippon Ink), Fluorad FC430, 431 (made by Sumitomo 3M), Fluorochemical surfactants, such as Asahi guard AG710, the Sir chlorofluocarbon S-382, SC-101, 102, 103, 104, 105 (made by Asahi Glass), etc. can be mentioned. That below the amount part of duplexs carries out to solid content 100 weight section of a hardenability resin composition makes loadings of these surface-active agents one or less weight section desirable still more preferably.

[0152]It is added in order to improve adhesion with an adjoining substrate and another coating layer, for example, the silane coupling agent can illustrate vinylsilane, an acrylic silane, epoxysilane, an aminosilane, etc. More specifically, vinyl trichlorosilan, vinyltris (beta-methoxyethoxy) Silang, vinyltriethoxysilane, vinyltrimetoxysilane, etc. can be used as vinylsilane. As an acrylic silane, gamma-methacryloxpropyl trimethoxy silane, gamma-methacryloxypropylmethyldimethoxysilane, etc. can be used. As epoxysilane, beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, gamma-glycidoxypropyltrimetoxysilane, gamma-glycidoxypropylmethyldietoxysilane, etc. can be used. Furthermore as an aminosilane, N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyl methyl trimetoxysilane, gamma-aminopropyl triethoxysilane, N-phenyl-gamma-aminopropyl trimethoxysilane, etc. can be used. As other silane coupling agents, gamma-mercapto propyltrimethoxysilane, gamma-chloropropyltrimetoxysilane, gamma-chloropropyl methyl dimethoxysilane, gamma-chloropropyl methyldiethoxysilane, etc. can be used.

[0153]In a hardenability resin composition of this invention, a solvent usually contains in consideration of paint-izing and spreading fitness. As an usable solvent, for example Methyl alcohol, ethyl alcohol, Alcohols solvents, such as N-propyl alcohol and i-propyl alcohol; Methoxy alcohol, Cellosolve Solvents, such as ethoxyalcohol; Methoxyethoxy ethanol, Carbitol system solvents, such as ethoxyethoxyethanol; Ethyl acetate, Butyl acetate, methoxy methyl propionate, and ethoxyethyl propionate, Ester solvents, such as ethyl lactate; Acetone, methyl isobutyl ketone, Ketones, such as cyclohexanone; Methoxy ethyl acetate, Cellosolve acetate system solvents, such as ethoxyethyl acetate and ethylcellosolve acetate; Methoxy ethoxyethyl acetate, Carbitol acetate system solvents, such as ethoxyethoxyethyl acetate; Diethylether, Ethyleneglycol dimethyl ether, diethylene glycol dimethyl ether, Ethers solvents, such as a tetrahydrofuran; Lactone system solvent; benzene, such as aprotic amide solvent; gamma-butyrolactone, such as N.N-dimethylformamide, N,N-dimethylacetamide, and N-methyl pyrrolidone,

toluene, xylene, Unsaturation hydrocarbon system solvents, such as naphthalene; organic solvents, such as saturated hydrocarbon system solvents, such as N-heptane, N-hexane, and N-octane, can be illustrated. In these solvents, methoxy ethyl acetate, ethoxyethyl acetate, Cellosolve acetate system solvents, such as ethylcellosolve acetate; Methoxy ethoxyethyl acetate, Carbitol acetate system solvents, such as ethoxyethoxyethyl acetate; Ethyleneglycol dimethyl ether, Ethers solvents, such as diethylene glycol dimethyl ether and propylene glycol diethylether; ester solvents, such as methoxy methyl propionate, ethoxyethyl propionate, and ethyl lactate, are used especially suitably. Preferably especially MBA (acetic acid-3-methoxy butyl, $CH_3CH(OCH_3)CH_2CH_2OCOCH_3$), PGMEA (propylene-glycol-monomethyl-ether acetate.) $CH_3OCH_2CH(CH_3)OCOCH_3$, What mixed DMDG (diethylene glycol dimethyl ether, $H_3COC_2H_4OCH_3$) or these can be used, and solids concentration is prepared to 5 to 50% of the weight using these.

[0154]While manufacturing a hardenability resin composition of this invention, as law, first, each monomer is made to react in a solvent for composition like said MBA (acetic acid-3-methoxy butyl), and a raw material polymer is compounded. Next, it is dropped, a radical polymerization nature group content isocyanate compound is made to react to a solution of an obtained raw material polymer so that equivalent ratio (NCO/OH) of an isocyanate group to a hydroxyl group contained in a main chain of a raw material polymer may become 1.0 or more, and hardening resin (photoresist polymer) is made to generate. When especially transparency or diactinism of resin is required, As mentioned above, a raw material polymer is manufactured using a polymerization initiator of non-nitrile system azo or a peroxide system, and a radical polymerization nature group content isocyanate compound is introduced using polymerization inhibitor expressed with a formula (9) or a formula (15). And alcohol is added, and at 30-170 **, hardening resin which carried out alcoholic processing is heated during less than 72 hours to reaction mixture containing the hardening resin concerned, and is ripened to it. Then, reaction mixture is mixed to a resist solvent like MBA, PGMEA, and DMDG with other resist materials. Usually let solids concentration in a hardenability resin composition be 5 to 85% of the weight of a range.

[0155]when hardening resin (photoresist polymer) of this invention is mixed with other coating materials and a solvent is dissolved or distributed, compared with an independent solution of hardening resin, a thickening phenomenon is the much more -- it becomes remarkable. For this reason, when mixing hardening resin with other materials and preparing a hardenability resin composition, after carrying out alcoholic processing of the hardening resin, fixed-time-neglecting it, or heating and making it fully ripe, especially mixing with other materials is preferred.

[0156]As for alcohol made to react to hardening resin, it is preferred to have the boiling point near [as possible] a solvent for preparing coating liquid or as near a vapor rate as possible, and especially its thing with both near boiling point and vapor rate is preferred. In a difference of the boiling point of alcohol, and the boiling point of a solvent for coating liquid, a difference of less than 40 ** and/or a vapor rate of alcohol, and a vapor rate of a solvent for coating liquid is especially more specifically 90 less than 75 **. [n-BuOAc=100] Less than, it is especially 30. [n-

BuOAc=100] It is preferred that it is less than. Since alcohol also evaporates together with a solvent for coating liquid even if alcohol remains in a hardenability resin composition when the boiling point or a vapor rate of alcohol is as near as a solvent of coating liquid, it is hard to produce coating unevenness. Since a pentanol has the boiling point and a vapor rate near PGMEA or DMDG, it is preferred to carry out alcoholic processing of the hardening resin using a pentanol, and to prepare a hardenability resin composition after that, using MBA, PGMEA, DMDG (s), or these mixtures as a resist solvent. Since a pentanol has the boiling point and a vapor rate also near MBA, MBA is used as a diluting solvent at the time of composition, alcoholic processing is carried out using a pentanol, and it is still more preferred especially to prepare a hardenability resin composition, using MBA, PGMEA, DMDG(s), or these mixtures as a resist solvent.

[0157]Thus, high sensitivity hardening resin is used as the main ingredients, exposure sensitivity is dramatically high, a hardenability resin composition of this invention obtained is a small light exposure, or it is possible to make it harden by very short exposure time. Therefore, business time of pattern formation can be shortened and energy for exposure can be saved.

[0158]In this invention, following methods can estimate exposure sensitivity of a hardenability resin composition. First, apply a hardenability resin composition on a substrate, it is made to dry if needed, and a coating film is formed. Here, if it does not interfere with a series of pattern formation processes, such as exposure and development, like a clear glass board as a substrate, it can be used especially satisfactorily. Although restriction in particular does not have thickness of a coating film, it is usually considered as a thickness of about 1-10 micrometers. It is relevant conditions and this coating film is prebaked, for example for 1 to 10 minutes at 70-150 **. A coating film is exposed with known irradiation intensity after prebaking, and thickness is measured. Let thickness measured in this stage be "the thickness before development."

[0159]Next, a coating film is developed by contacting a prebaked coating film to a suitable developer, dissolving an unexposed part, removing, and washing an exposure part which remained if needed. Here, a presentation of a developer and conditions of development are appropriately chosen according to a hardenability resin composition examined. It cannot be overemphasized that what hardly dissolves an exposure part (hardened portion) of a hardenability resin composition, but can dissolve an unexposed part thoroughly as a developer is preferred. And it is relevant conditions and postbake of the developed coating film is carried out, for example for 20 to 80 minutes at 180-280 **. Thickness of a coating film is measured after postbake and it is considered as "thickness after the last hardening."

[0160]Thus, according to a following formula, a remaining rate of membrane is calculated from measured thickness before development, and thickness after the last hardening.

[0161]remaining-rate-of-membrane (%) =(front [after / the last hardening / thickness (micrometer) / development] thickness (micrometer)) x100 -- on the other hand, it applies on a substrate like the above and the same hardenability resin composition is dried, it prebakes and a coating film for references is formed. This coating film for references is exposed with irradiation intensity which the coating film concerned hardens thoroughly, and thickness is measured. Let thickness

measured in this stage be "full exposure thickness." Next, after carrying out postbake by same method as a sample, without development carrying out a coating film which carried out full exposure, it measures by same method as having mentioned thickness of an obtained film above, and is considered as "the last thickness without a developing process." And according to a following formula, a reference remaining rate of membrane is calculated from full exposure thickness and the last thickness without a developing process which were measured.

[0162]reference remaining-rate-of-membrane (%) =(last thickness (micrometer) / full exposure thickness without developing process (micrometer)) x100 -- a remaining rate of membrane and a reference remaining rate of membrane being computed by doing in this way, and, A remaining rate of membrane determines the smallest light exposure that became equal to a reference remaining rate of membrane as 1% of an error span as the minimum light exposure of a hardenability resin composition. It can be estimated that sensitivity is high, so that this minimum light exposure is small.

[0163]According to this invention, a thing [a thing] the minimum light exposure of below 50 mJ/cm^2 determined by doing in this way is [below 100 mJ/cm^2] 35 mJ/cm^2 still more preferably preferably of obtaining a hardenability resin composition of high sensitivity very much is possible.

[0164]A hardenability resin composition of this invention is suitable for forming a columnar spacer for maintaining a protective layer which covers a coloring layer of a light filter, and the coloring layer concerned, and a cell gap of a liquid crystal panel.

[0165]A light filter is provided with a protective film formed so that a black matrix formed in a transparent substrate by a predetermined pattern, a coloring layer formed by a predetermined pattern on the black matrix concerned, and the coloring layer concerned might be covered. A transparent electrode for a liquid crystal drive may be formed if needed on a protective film. According to a field in which a black matrix layer was formed, a columnar spacer may be formed on a transparent electrode plate, a coloring layer, or a protective film.

[0166]It comes to arrange a coloring layer with a gestalt of a request of a red pattern, a green pattern, and a blue pattern of mosaicism, a stripe type, a triangle type, a 4-pixel arrangement type, etc., and a black matrix is provided in a predetermined region of the outside of between each coloring pattern and a coloring stratification field. Although a coloring layer can be formed by various methods, it is preferred to form by a pigment dispersion method using the above-mentioned hardenability resin composition. That is, the above-mentioned hardenability resin composition is made to distribute a color pigment, a coating material is prepared, and it applies to the whole surface side of a transparent substrate, and exposes by irradiating with ultraviolet rays via a photo mask, and a coloring layer can be formed by carrying out heat cure with clean oven etc. after alkaline development. A coloring layer is usually formed in a thickness of about 1.5 micrometers.

[0167]Even if any of a staining technique, a pigment dispersion method, print processes, and an electrodeposition process are used for a black matrix, it can be formed, and it may be formed by chromium vacuum evaporation etc.

[0168]The protective film can apply coating liquid of the above-mentioned hardenability resin composition by methods, such as a spin coater, a roll coater, a spray, and printing, and can form it. A protective film is formed in a thickness of about 2 micrometers, for example. When

using a spin coater, number of rotations is set up within the limits of 500 - 1500 revolution per minute. A coating film of a hardenability resin composition is exposed by irradiating with ultraviolet rays via a photo mask, and after alkaline development, heat cure of it is carried out with clean oven etc., and it turns into a protective film.

[0169]A transparent electrode on a protective film Indium tin oxide (ITO), a zinc oxide (ZnO), Tin oxide (SnO) etc. are formed by general methods, such as sputtering process, a vacuum deposition method, and a CVD method, using those alloys, and let them be a predetermined pattern by use of etching or a jig using photoresist if needed. about 20-500 nm of thickness of this transparent electrode shall be about 100-300 nm preferably -- things can be carried out.

[0170]Coating liquid of the above-mentioned hardenability resin composition is applied by methods, such as a spin coater, a roll coater, a spray, and printing, it exposes by UV irradiation through a photo mask, and a columnar spacer on a transparent electrode can also be formed by carrying out heat cure with clean oven etc. after alkaline development. A columnar spacer is formed in a height of about 5 micrometers, for example. What is necessary is just to set up number of rotations of a spin coater as well as a case where a protective film is formed, within the limits of 500 - 1500 revolution per minute.

[0171]Thus, a liquid crystal panel is obtained by forming an orienting film in the inner surface side of a manufactured light filter, making it counter with an electrode substrate, and filling and sealing a liquid crystal to an interval part.

[0172]

[Example](Example 1)

(Composition of high sensitivity resin (1'))

following daily dose and benzyl methacrylate (BzMA): -- 250g and styrene (St):350g and, and acrylic acid (AA):200g and, and 2-hydroxyethyl methacrylate (HEMA): -- 200 g of benzyl methacrylate. Styrene, acrylic acid, and 2-hydroxyethyl methacrylate with 5 g of azobisisobutyronitrile (azobisuisobutironitoriru). The solution which dissolved in 650 g of acetic acid-3-methoxy butyl was trickled and polymerized over 6 hours in the polymerization tank into which 1000 g of acetic acid-3-methoxy butyl was put at 100 **, and the solution of the raw material polymer was obtained.

[0173]Next, after carrying out package addition of the mixture (the following presentation, 2-methacryloiloxy-ethyl isocyanate (MOI):240g, lauric acid dibutyl tin:1g, acetic acid-3-methoxybutyl:2260g, and hydroquinone (HQ):2.5g) at **** of the obtained raw material polymer, Heating stirring was carried out and the reaction mixture containing the high sensitivity hardening resin (1') before alcoholic processing was obtained. It was made to react monitoring advance of a reaction by IR (infrared absorption spectrum) until the peak by the isocyanate group of 2200-cm^{-1} disappeared.

[0174]The preparation rate (mol %) of each monomer is as follows. benzyl methacrylate: -- styrene: -- acrylic acid: -- 2-hydroxyethyl methacrylate: -- 2-methacryloiloxy-ethyl isocyanate =13.3:31.7:26.2:14.4:14.4. The equivalent ratio (NCO/OH) of the isocyanate group of 2-methacryloiloxy-ethyl isocyanate to the hydroxyl group of 2-hydroxyethyl methacrylate is 1.0.

[0175]The solid content of the obtained reaction mixture was 25.5 % of the weight, and viscosity was 77.3 mPa-s/25 **. After applying the obtained reaction mixture on a glass plate, decompress overnight, it was

made to dry at a room temperature, and the solvent was removed. The acid value of the obtained solid was 125.5 mgKOH/g, and weight average molecular weight was 42,500.
[0176]Various physical properties were measured by the following method.
[0177]a. Solid content: After weighing precisely and putting the reaction mixture 0.7-0.8g into the aluminum pan and making it dry with hot air drying equipment at 105 ** for 6 to 7 hours, dry weight was weighed precisely promptly and the rate of dry weight over reaction mixture weight was searched for.
[0178]b. Viscosity (mPa-s/25**) : It measured by 60 rotations using rotor No.1 using the Brookfield viscometer.
[0179]c. Acid value: The sample was dissolved in acetone and it asked by carrying out a neutralization titration by NaOH of 1/10N by using cresol red as an indicator.
[0180]d. Hydroxyl value: It asked from the weight of KOH required to neutralize the acid value which can acetylate 1 g of dried solid content.
[0181]e. Weight average molecular weight: A GPC measuring condition and a column column: Schodex GPC KF-805L (made by Showa Denko K.K.)
Flow: 1.0 (ml/min.)
temperature: -- 40 ** eluate: -- tetrahydrofuran detector: -- RI [0182] (Alcoholic processing of high sensitivity hardening resin (1')) After [10 % of the weight] adding 1-pentanol so that it may become comparatively, it was made to ripe to the reaction mixture (acetic acid-3-methoxy butyl solution of 25.5 % of the weight of solid content) containing high sensitivity hardening resin (1'). At 90 **, a part of reaction mixture which added 1-pentanol carried out heating stirring for 11 hours, and it was ripened. At 70 **, another part carried out heating stirring for 30 hours, and was ripened. After the completion of aging, it is an acid anhydride group in both cases. [1783 - 1822-cm^{-1}] /benzene ring It checked by FT-IR spectrum that the surface ratio expressed with [683 - 721-cm^{-1}] had become 0.03 or less. Thus, the reaction mixture containing the high sensitivity hardening resin (1) which is an alcoholic processing body of high sensitivity hardening resin (1') was obtained. The solids concentration of the obtained reaction mixture was 23.2 % of the weight, and viscosity was 49.5 mPa-s/25 **.
[0183](Preparation of a hardenability resin composition (1))
the reaction mixture (23.2 % of the weight of solid content):59.0 weight section and dipentaerythritol pentaacrylate (the Sartomer make.) containing each material and the above-mentioned high sensitivity resin (1) of the following daily dose SR399:11.0 weight section and polyglycidyl ether of o-cresol-form aldeyde novolac (oil recovery shell epoxy company make.) Epicoat 180S70:15.0 weight section and 2-methyl-1-. (4-methylthio phenyl)-2-morpholinopropanone 1:. The 2.1 weight section and 2,2'-bis(o-chlorophenyl)-4,5,4',5'-tetraphenyl- 1, 2'-biimidazole : 1.5 weight sections, diethylene-glycol-dimethyl-ether:59.0 weight section, and acetic acid-3-methoxy butyl:7.4 weight section is stirred and mixed at a room temperature, The hardenability resin composition (1) was obtained.
[0184](Example 2) Except having changed the equivalent ratio of the isocyanate group of 2-methacryloiloxy-ethyl isocyanate to the preparation rate of each monomer, and the hydroxyl group of 2-hydroxyethyl methacrylate as follows, like Example 1 Composition of resin, alcoholic processing, The constituent was prepared and the

hardenability resin composition (2) containing high sensitivity hardening resin (2) was obtained.
[0185]- BzMA:St:AA:HEMA:MOI=12.9:25.6:25.3:16.4:19.7andNCO/OH=1.2 [0186](Example 3) Except having changed the equivalent ratio of the isocyanate group of 2-methacryloiloxy-ethyl isocyanate to the preparation rate of each monomer, and the hydroxyl group of 2-hydroxyethyl methacrylate as follows, like Example 1 Composition of resin, alcoholic processing, The constituent was prepared and the hardenability resin composition (3) containing high sensitivity resin (3) was obtained.
[0187]- BzMA:St:AA:HEMA:MOI=12.3:24.4:24.1:15.7:23.5andNCO/OH=1.5 [0188](Example 4) About the polymerization initiator at the time of preparing a raw material polymer, they are the dimethyl 2 of tales doses [azobisuisobutironitoriru / 5 g of / (nitrile system)], and 2'-azobis (2-methylpropionate) (). [DAMP and] Polymerization inhibitor at the time of changing into a non-nitrile system and making 2-methacryloiloxy-ethyl isocyanate react, Except having changed into tales doses of 3,5 di-tert-butyl-4-hydroxy toluene (BHT) from 2.5 g of hydroquinone (HQ), composition of resin, alcoholic processing, and preparation of a constituent were performed like Example 1, and the hardenability resin composition (4) containing high sensitivity resin (4) was obtained.
[0189](Example 5) Except having made it react to the solution of a raw material polymer by dropping 2-methacryloiloxy-ethyl isocyanate, it carried out like Example 4 and the hardenability resin composition (5) containing high sensitivity resin (5) was obtained.
[0190](Example 6) Except having changed the equivalent ratio of the isocyanate group of 2-methacryloiloxy-ethyl isocyanate to the preparation rate of each monomer, and the hydroxyl group of 2-hydroxyethyl methacrylate as follows, like Example 1 Composition of resin, alcoholic processing, The constituent was prepared and the hardenability resin composition (6) containing high sensitivity resin (6) was obtained.
[0191]- BzMA:St:AA:HEMA:MOI=0:35.7:24.0:18.3:21.9andNCO/OH=1.2 [0192](Example 7) Except having made it react to the solution of a raw material polymer by dropping 2-methacryloiloxy-ethyl isocyanate, it carried out like Example 6 and the hardenability resin composition (7) containing high sensitivity resin (7) was obtained.
[0193](Example 8) Except having changed the equivalent ratio of the isocyanate group of 2-methacryloiloxy-ethyl isocyanate to the preparation rate of each monomer, and the hydroxyl group of 2-hydroxyethyl methacrylate as follows, like Example 1 Composition of resin, alcoholic processing, The constituent was prepared and the hardenability resin composition (8) containing high sensitivity resin (8) was obtained.
[0194]- BzMA:St:AA:HEMA:MOI=0:38.2:21.2:18.5:22.2andNCO/OH=1.2 [0195](Example 9) Except having made it react to the solution of a raw material polymer by dropping 2-methacryloiloxy-ethyl isocyanate, it carried out like Example 8 and the hardenability resin composition (9) containing high sensitivity resin (9) was obtained.
[0196](Example 10) About the polymerization initiator at the time of preparing a raw material polymer, they are the dimethyl 2 of tales doses [azobisuisobutironitoriru / 5 g of / (nitrile system)], and 2'-azobis (2-methylpropionate) (). [DAMP and] Polymerization inhibitor at the time of changing into a non-nitrile system and making 2-methacryloiloxy-ethyl isocyanate react, It changes into tales doses of 3,5 di-tert-butyl-4-

hydroxy toluene (BHT) from 2.5 g of hydroquinone (HQ), And except having made it react to the solution of a raw material polymer by dropping 2-methacryloiloxy-ethyl isocyanate, it carried out like Example 6 and the hardenability resin composition (10) containing high sensitivity resin (10) was obtained.

[0197](Example 11) About the polymerization initiator at the time of preparing a raw material polymer, they are the dimethyl 2 of tales doses [azobisuisobutironitoriru / 5 g of / (nitrile system)], and 2'-azobis (2-methylpropionate) (). [DAMP and] Polymerization inhibitor at the time of changing into a non-nitrile system and making 2-methacryloiloxy-ethyl isocyanate react, It changes into tales doses of 3,5 di-tert-butyl-4-hydroxy toluene (BHT) from 2.5 g of hydroquinone (HQ), And except having made it react to the solution of a raw material polymer by dropping 2-methacryloiloxy-ethyl isocyanate, it carried out like Example 8 and the hardenability resin composition (11) containing high sensitivity resin (11) was obtained.

[0198](Example 12)

(A photo-setting resin constituent (12) and preparation of (12')) the reaction mixture (23.2 % of the weight of solid content):97.0 weight section and dipentaerythritol pentaacrylate (the Sartomer make.) containing the high sensitivity resin (1) obtained in each material and Example 1 of the following daily dose SR399:18.0 weight section and polyglycidyl ether of o-cresol-form aldeyde novolac (oil recovery shell epoxy company make.) Epicoat 180S70:. 25.0 weight section and 2-benzyl-2-N,N-dimethylamino 1-(4-morpholinophenyl)-1-butanone : The 2.5 weight section and 2,2'-bis(o-chlorophenyl)-4,5,4',5'-tetraphenyl- 1, 2'-biimidazole :. 2.0 weight section and polyoxyethylene octylphenyl ether (Nonion HS-210, Nippon Oil & Fats Co., Ltd. make): -- 3.6 weight section and propylene-glycol-monomethyl-ether acetate: -- 59.0 weight sections were stirred and mixed at the room temperature, and the photo-setting resin constituent (12) was obtained.

[0199]It replaced with the reaction mixture which contains high sensitivity resin (1) in the above-mentioned presentation, and the photo-setting resin constituent (12') was obtained using the reaction mixture containing the high sensitivity resin (1') which was obtained in Example 1 and which has not carried out alcoholic processing.

[0200](Retention test) The viscosity of the above-mentioned photo-setting resin constituent (12) and a photo-setting resin constituent (12'), When the Brookfield viscometer was used and measured immediately after preparation, the photo-setting resin constituent (12') was 20.0 mPa-s/25 **, and the photo-setting resin constituent (12) which carried out alcoholic processing was 18.5 mPa-s/25 **.

[0201](Example 13)

(Formation of a black matrix) On a 1.1-mm-thick glass substrate (AL material by Asahi Glass Co., Ltd.), following daily dose and black pigment: -- 23 weight section and polymers dispersing agent (big KEMI Japan Disperbyk 111): -- amount part of duplexs, and solvent (diethylene glycol dimethyl ether): -- the ingredient of 75 weight sections was mixed, it fully distributed in the sand mill, and black pigment dispersion liquid were prepared.

[0202]Next, the ingredient of hardenability resin composition (1):20 weight section and diethylene-glycol-dimethyl-ether:30 weight section of the following daily dose, and above-mentioned black pigment dispersion-liquid:61 weight section and example 1 was fully mixed, and the constituent for light shielding layers was obtained.

[0203]And applied the above-mentioned constituent for light shielding layers by the spin coater on the 1.1-mm-thick glass substrate (AL material by Asahi Glass Co., Ltd.), it was made to dry for 3 minutes at 100 **, and the light shielding layer of about 1 micrometer of thickness was formed. After exposing the light shielding layer concerned to a shielding pattern with an extra-high pressure mercury lamp, it is developed with a potassium hydroxide solution 0.05%.
Then, the black matrix was formed in the field which should heat-treat by neglecting a substrate for 30 minutes in 180 ** atmosphere, and should form a shade part.

[0204](Formation of a coloring layer) On the substrate which formed the black matrix as mentioned above, the red-induration nature resin composition of the following presentation was applied by the spin coating method (coating thickness of 1.5 micrometers), and it dried for 30 minutes in 70 ** oven after that.
[0205]Subsequently, only the field which arranges a photo mask in distance of 100 micrometers from the coating film of a red-induration nature resin composition, and is equivalent to the formation area of a coloring layer using a 2.0-kW extra-high pressure mercury lamp by a proximity aligner was irradiated with ultraviolet rays for 10 seconds. Subsequently, it was immersed for 1 minute into a 0.05% potassium hydroxide solution (23 ** of solution temperature), alkaline development was carried out, and only the uncured part of the coating film of a red-induration nature resin composition was removed. Then, the red relief pattern was formed in the field which should heat-treat by neglecting a substrate for 30 minutes in 180 ** atmosphere, and should form a red picture element.
[0206]Next, the green relief pattern was formed in the field which should form a green picture element at the same process as red relief pattern formation using the green hardenability resin composition of the following presentation.
[0207]Using the blue hardenability resin composition of the following presentation, the blue relief pattern was formed in the field which should form a blue pixel at the same process as red relief pattern formation, and the coloring layer which consists of three colors of red (R) green (G) blue (B) was created.
[0208]a. presentation, C.I. pigment red 177:10 weight section, and polysulfone acid type polymers dispersing agent: -- The hardenability resin composition (1):5 weight section and acetic acid of 3 weight sections and Example 1-3-methoxy -- butyl:82 weight section [of a red-induration nature resin composition] [0209]b. the presentation of a green hardenability resin composition, and C.I. pigment green 36:10 weight section and polysulfone acid type polymers dispersing agent: -- The hardenability resin composition (1):5 weight section and acetic acid of 3 weight sections and Example 1-3-methoxy -- butyl:82 weight section
[0210]c. presentation and C.I. pigment blue: -- 10 weight section and polysulfone acid type polymers dispersing agent: -- The hardenability resin composition (1):5 weight section and acetic acid of 3 weight sections and Example 1-3-methoxy -- butyl:82 weight section [of a blue hardenability resin composition] [0211](Example 14)
(Spreading of a hardenability resin composition (1)) On the glass substrate which formed the coloring layer in Example 13, the hardenability resin composition (1) of Example 1 was applied and dried by the spin coating method, and the coating film of 2 micrometers of dry

membrane thickness was formed.
[0212](Formation of a protective film) Only the field which arranges a photo mask in distance of 100 micrometers from the coating film of a hardenability resin composition (1), and is equivalent to the formation area of a coloring layer using a 2.0-kW extra-high pressure mercury lamp by a proximity aligner was irradiated with ultraviolet rays for 10 seconds. Subsequently, it was immersed for 1 minute into a 0.05% potassium hydroxide solution (23 ** of solution temperature), alkaline development was carried out, and only the uncured part of the coating film of a hardenability resin composition was removed. Then, it heat-treated by neglecting a substrate for 30 minutes in 200 ** atmosphere, the protective film was formed, and the light filter of this invention was obtained.
[0213](Example 15)
(Spreading of a photo-setting resin constituent (12)) On the glass substrate which formed the coloring layer in Example 13, the hardenability resin composition (12) obtained in Example 12 was applied and dried by the spin coating method, and the coating film of 5 micrometers of dry membrane thickness was formed.
[0214](Formation of a spacer) In distance of 100 micrometers, from the coating film of a hardenability resin composition (12). The photo mask designed form predetermined shape, a size, and the exposure pattern that has an interval has been arranged, and only the formation area of the spacer on a black matrix was irradiated with ultraviolet rays for 10 seconds using a 2.0-kW extra-high pressure mercury lamp by the proximity aligner. Subsequently, it was immersed for 1 minute into a 0.05% potassium hydroxide solution (23 ** of solution temperature), alkaline development was carried out, and only the uncured part of the coating film of a photo-setting resin constituent was removed. Then, it heat-treated by neglecting a substrate for 30 minutes in 200 ** atmosphere, the fixing spacer was formed, and the light filter of this invention was obtained.
[0215](Example 16) Argon and oxygen were made into discharge gas with the substrate temperature of 200 **, with DC magnetron sputtering method, ITO was targeted on the surface containing the fixing spacer of the light filter obtained in Example 15, and the transparent electrode film was formed on it. Then, the orienting film which consists of polyimide was further formed on the transparent electrode film.
[0216]Subsequently, at 150 **, it joined having put the pressure of 0.3 kg/cm^2, cell **** of the above-mentioned light filter and the glass substrate in which TFT was formed was carried out, using an epoxy resin as a sealant, the TN liquid crystal was enclosed, and the liquid crystal display of this invention was produced.
[0217](Example 17) On the coloring layer concerned of the glass substrate which formed the coloring layer in Example 13, Or on the protective film concerned of the light filter which formed the coloring layer and the protective film in Example 14, argon and oxygen were made into discharge gas with the substrate temperature of 200 **, with DC magnetron sputtering method, ITO was targeted and the transparent electrode film was formed. Then, the spacer was formed at the same process as Example 15 on the transparent electrode film, the orienting film which consists of polyimide further was formed, and the light filter was obtained.
[0218]Subsequently, at 150 **, it joined having put the pressure of 0.3 kg/cm^2, cell **** of the above-mentioned light filter and the glass

substrate in which TFT was formed was carried out, using an epoxy resin as a sealant, the TN liquid crystal was enclosed, and the liquid crystal display of this invention was produced.

[0219](Analysis by ^{1}H-NMR) 5 g of reaction mixture (acetic acid-3-methoxy butyl solution of 23.2 % of the weight of solid content) containing the high sensitivity resin (1) which was obtained in Example 1 and which carried out alcoholic processing, A small quantity was dropped every by the syringe, stirring in 300 g of isopropanol, after diluting with 5 g of tetrahydrofurans. Supernatant liquid was thrown away, and again, the solid content which solidified in the bottom was thoroughly melted in a 5-g tetrahydrofuran, and was dropped at it in a similar manner in 300 g of isopropanol. The obtained solid content was thoroughly melted in a 20-g tetrahydrofuran, and was dropped at it similarly in 300 g of hexane. The depositing solid was filtered, reduced pressure drying was carried out at the room temperature overnight, and the sample was prepared. The weight average molecular weight of the obtained sample was 94,000. This sample is thoroughly dissolved in heavy DMSO, and the result of having conducted ^{1}H-NMR analysis is shown below.

[0220]

^{1}H-NMR (DMSO-d) sigmappmsigma0.2 - 1.1 (m, 12H)
sigma1.1-1.8 (m, 19H)
sigma1.85 (s, 3H)
sigma3.27 (b, 2H)
sigma3.51 (b, 2H)
sigma3.90 (b, 2H)
sigma4.08 (b, 2H)
sigma4.75 (b, 1H)
sigma4.90 (b, 2H)
sigma5.63 (s, 1H)
sigma6.05 (s, 1H)
sigma7.11 (b, 23H)
sigma7.31 (b, 6H)
sigma12.04 (b, 2H)

[0221]From ^{1}H-NMR analysis, the unit ratio (mole ratio) of each constitutional unit in the high sensitivity resin (1) which carried out reprecipitation purification treatment, benzyl methacrylate: -- styrene: -- acrylic acid: -- 2-hydroxyethyl methacrylate: -- it was 2-methacryloiloxy-ethyl isocyanate =2:5:4:2:1. In the refined high sensitivity resin (1), the introduction amount (mol) of 2-methacryloiloxy-ethyl isocyanate (MOI) to 100 mol of constitutional units of a main chain was 8.02 mol.

[0222]Reprecipitation refining of the reaction mixture which contains the high sensitivity resin (2) thru/or (11) obtained in other examples by the same method was carried out, and ^{1}H-NMR analyzed. An analysis result is shown in the 1st table with the result of the below-mentioned sensitivity evaluation.

[0223](Evaluation of sensitivity) On the glass substrate of 10-cm drawing, the hardenability resin composition (1) obtained in Example 1 was applied and dried by the spin coater (product made from MIKASA, and formal 1H-DX2), and the coating film of 2 micrometers of dry membrane thickness was formed. 90 ** of this coating film was heated for 3 minutes on the hot plate. By UV aligner (the product made from a great Japan screen, formal MA 1200) which has arranged the photo mask in distance of 100 micrometers from the coating film, and equipped with a 2.0-kW extra-high pressure mercury lamp after heating. Each of each

field which divided the same coat into four equally was irradiated with ultraviolet rays by the intensity (405-nm illumination conversion) of 25, 35, 50, and 100 mJ/cm^2.

[0224]After the exposure of ultraviolet rays, the coating film was shaved [fields / four / these / each] to the rectangular shape whose sizes are about 1 mm x 3 mm, the glass substrate was exposed selectively, the thickness of each irradiation area was measured with the sensing pin type surface roughness measuring device (the Japanese Anelva CORP. make, Dektak 1600), and it was considered as the thickness before development.

[0225]Subsequently, it is a spin development machine () about 0.05wt% of a potassium hydroxide solution to the exposure part of a coating film. [Applied Process Technology, INK and] MODEL: It sprinkled for 60 seconds in 915, and negatives were developed by dissolving an unexposed part, removing and rinsing the exposure part which remained for 60 seconds with pure water. The film of the exposure part was heated for 30 minutes at 200 ** after development with clean oven (the OSHITARI LABORATORY, INC. make, SCOV-250 Hy-So). And the thickness of each field of the obtained film was measured by the same method as having mentioned above, and was made into the thickness after the last hardening.

[0226]Thus, according to the following formula, the remaining rate of membrane was calculated from the measured thickness before development, and the thickness after the last hardening.

[0227]remaining-rate-of-membrane (%) =(front [after / the last hardening / thickness (micrometer) / development] thickness (micrometer)) x100 -- on the other hand, the reference remaining rate of membrane was determined as follows. First, except having exposed by the intensity of 100 mJ/cm^2 all over the coating film, it is the same method as a sample and the full exposure thickness of the hardenability resin composition (1) was measured. Next, after carrying out only heating by the same method as a sample, without development carrying out the 100-mJ/cm-^{2}-exposed coating film, it measured by the same method as having mentioned the thickness of the obtained film above, and was considered as the last thickness without a developing process. And according to the following formula, the reference remaining rate of membrane was calculated from the full exposure thickness and the last thickness without a developing process which were measured.

[0228]Reference remaining rate of membrane (%) =(last thickness (micrometer) / full exposure thickness without developing process (micrometer)) x100 [0229]Thus, the computed remaining rate of membrane determined the smallest light exposure that became equal to a reference remaining rate of membrane as 1% of an error span as the minimum light exposure of the hardenability resin composition (1).

[0230]By the same method as having mentioned above, the hardenability resin composition (2) obtained in other examples thru/or the coating film of (11) were formed, front [development] thickness, the thickness after the last hardening, full exposure thickness, and the last thickness without a developing process were measured, and each hardenability resin composition (2) thru/or the minimum light exposure of (11) were determined.

[0231]Thus, the minimum light exposure was determined about each hardenability resin composition (1) thru/or (11). A result is shown in the 1st table.

[0232]

[Table 1]

第１表（１／２）

	組成比 BzMA:St:AA:HEMA:MOI	NCO /OH	重合開始剤 ／重合禁止剤	滴下の有無
高感度樹脂／硬化性樹脂組成物(1)	13.3:31.7:26.2:14:4	1.0	AIBN/HQ	無し
高感度樹脂／硬化性樹脂組成物(2)	12.9:25.6:25.3:16.4:19.7	1.2	AIBN/HQ	無し
高感度樹脂／硬化性樹脂組成物(3)	12.3:24.4:24.1:15.7:23.5	1.5	AIBN/HQ	無し
高感度樹脂／硬化性樹脂組成物(4)	（１）と同じ	1.0	DAMP/BHT	無し
高感度樹脂／硬化性樹脂組成物(5)	（４）と同じ	1.0	DAMP/BHT	滴下
高感度樹脂／硬化性樹脂組成物(6)	0:35.7:24.0:18.3:21.9	1.2	AIBN/HQ	無し
高感度樹脂／硬化性樹脂組成物(7)	（６）と同じ	1.2	AIBN/HQ	滴下
高感度樹脂／硬化性樹脂組成物(8)	0:38.2:21.2:18.5:22.2	1.2	AIBN/HQ	無し
高感度樹脂／硬化性樹脂組成物(9)	（８）と同じ	1.2	AIBN/HQ	滴下
高感度樹脂／硬化性樹脂組成物(10)	（６）と同じ	1.2	DAMP/BHT	滴下
高感度樹脂／硬化性樹脂組成物(11)	（８）と同じ	1.2	DAMP/BHT	滴下

[0233]

[Table 2]

第１表（２／２）

	1H-NMR (モル)	最低硬化露光量 (mJ)
高感度樹脂／硬化性樹脂組成物(1)	8.02	100
高感度樹脂／硬化性樹脂組成物(2)	12.0	50
高感度樹脂／硬化性樹脂組成物(3)	16.0	35
高感度樹脂／硬化性樹脂組成物(4)	8.07	50
高感度樹脂／硬化性樹脂組成物(5)	8.05	50
高感度樹脂／硬化性樹脂組成物(6)	18.7	50
高感度樹脂／硬化性樹脂組成物(7)	19.5	35
高感度樹脂／硬化性樹脂組成物(8)	19.5	50
高感度樹脂／硬化性樹脂組成物(9)	20.3	35
高感度樹脂／硬化性樹脂組成物(10)	18.7	35
高感度樹脂／硬化性樹脂組成物(11)	20.7	25

[0234](Evaluation of preservability) the alcohol obtained in Example 1 --

the reaction mixture containing unsettled high sensitivity resin (1') and the reaction mixture containing the high sensitivity resin (1) which carried out alcoholic processing were saved at refrigeration, the room temperature, and the elevated temperature. And the viscosity after the end of a retention period was measured using the Brookfield viscometer the same with having carried out immediately after preparation of each reaction mixture.

[0235]The hardenability resin composition (12') and the hardenability resin composition (12) which carried out alcoholic processing which are not processed [which was obtained in Example 12 / alcoholic] were saved at refrigeration and a room temperature. And the viscosity after the end of a retention period was similarly measured using the Brookfield viscometer.

[0236]The ratio of the viscosity after the end of a retention period to the viscosity immediately after preparation is shown in the 2nd table and the 3rd table.

[0237]

[Table 3]

第２表

	高感度樹脂（１）（アルコール処理）	高感度樹脂（１'）（未処理）
冷蔵保存（２週間）	1.001倍	1.011倍
室温保存（２週間）	1.008倍	1.172倍
加熱保存（70℃、1.5日）	1.020倍	1.500倍

[0238]

[Table 4]

第３表

	硬化性樹脂組成物（１２）（アルコール処理）	硬化性樹脂組成物（１２'）（未処理）
冷蔵保存（２週間）	1.032倍	1.049倍
室温保存（２週間）	1.064倍	1.208倍

[0239](Evaluation of transparency) The reaction mixture containing the high sensitivity resin (1) obtained in Example 1, That is, acetic acid-3-methoxy butyl was added and diluted to the reaction mixture after alcoholic processing, the 20wt% solution was prepared as resin solid content, it put into the quartz cell of 1-cm drawing, and light transmission was measured in 350-550 nm. The light transmission of the reaction mixture which similarly contains the high sensitivity resin (4) obtained in Example 4, and the reaction mixture containing the high sensitivity resin (5) obtained in Example 5 was measured. A measurement result is shown in the 4th table.

[0240]

[Table 5]

第４表

	組成比	重合開始剤／重合禁止剤	滴下の有無	360nm	400nm	485nm
高感度樹脂(1)	同一	AIBN/HQ	無し	24(%)	64(%)	66(%)
高感度樹脂(4)		DAMP/BHT	無し	70	87	94
高感度樹脂(5)		DAMP/BHT	滴下	35	73	90

[0241]
[Effect of the Invention]As explained above, the high sensitivity hardening resin provided by this invention, It has a main chain which consists of a constitutional unit which has an acidic functional group at least, and a constitutional unit which has a hydroxyl group, A radical polymerization nature group content isocyanate compound has the molecular structure in which said acidic functional group carries out an amide bond in part at least via the isocyanate group of the isocyanate compound concerned, and/or said hydroxyl group carries out a urethane bond in part at least, and. It is adjusted so that the charge of a radical polymerization nature group content isocyanate compound may convert into the equivalent ratio (NCO/OH) of the isocyanate group to the hydroxyl group of a main chain and may become 1.0 or more. The charge of the constitutional unit which has a hydroxyl group still more preferably on the basis of the whole quantity of each constitutional unit which constitutes the main chain and side chain of high sensitivity hardening resin is adjusted more than 14 mol %. Therefore, a lot of radical polymerization nature groups as a side chain of a photoresist polymer are contained, and sensitivity can be dramatically high and it can be made to harden to the inside of a short time with a small light exposure.
[0242]As for the high sensitivity hardening resin of this invention, alcoholic processing is performed if needed. Such an alcoholic processing body can cause neither increase of a molecular weight, nor the rise of viscosity easily, even if it dissolves or distributes a solvent, and it is dramatically extremely stable compared with an alcoholic unsettled object. Therefore, it excels in preservability when it prepares in a solution, and it also becomes possible to carry out long term storage at a room temperature. Since viscosity does not rise while in use, it is easy to deal with the solution of the alcoholic processing body concerned.
[0243]By using the polymerization initiator of non-nitrile system azo or a peroxide system, and preparing a raw material polymer, when manufacturing the high sensitivity hardening resin of this invention, and/. Or the hardening resin which was dramatically excellent in transparency is obtained by introducing a radical polymerization nature group content isocyanate compound using one of the polymerization inhibitor chosen from the compounds expressed with an above-mentioned formula (9) or formula (15). Since light fully reaches the inside of the coat of hardening resin when transparency is high, it contributes also to improvement in sensitivity.
[0244]Therefore, the resin composition of the photoresist which uses the hardening resin of this invention as the main ingredients can be stiffened to the inside of a short time with a light exposure high sensitivity and small. Since a viscosity rise cannot break out easily, the hardenability resin composition of this invention is highly preservable, and a coat and a pattern without coating nonuniformity are obtained. The hardenability

resin composition of this invention can be used also when high transparency is searched for.
[0245]And especially the hardenability resin composition of this invention is suitable as a photoresist material for forming the columnar spacer for maintaining the protective layer which covers the coloring layer of a light filter, and the coloring layer concerned, and the cell gap of a liquid crystal panel. That is, if the hardenability resin composition of this invention is used, the coloring layer, protective film, and columnar spacer which were uniform and were excellent in dimensional stability by the coating nature whose productivity was high, and which was excellent by high sensitivity can be formed, and, moreover, a demand of required transparency can also be filled for a coloring layer and a protective film.

[Translation done.]